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ON THE TWO ISOMERIC CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

BY IRA REMSEN.

An investigation of the anilides of orthosulphobenzoic acid by C. E. Coates and myself has shown that, when the chloride of the acid is treated with aniline, two products of the formula $C_{19}H_{16}N_2SO_3$ are formed, and that with meta- and para-toluidine similar products are formed. These isomeric substances are well characterized and easily obtained in pure condition. The simplest hypothesis to account for their existence is that they are derived from isomeric chlorides represented by the formulas

$$C_6H_4<\begin{matrix}COCl\\SO_2Cl\end{matrix} \text{ and } C_6H_4<\begin{matrix}CCl_2\\SO_2\end{matrix}>O,$$

corresponding to the symmetrical and unsymmetrical chlorides of phthalic acid, of which phthalyl chloride is believed to consist.

A subsequent investigation by E. P. Kohler and myself led to the conclusions that the chloride of orthosulphobenzoic acid is, in fact, a mixture of two substances, one a solid at ordinary temperatures, the other an uncrystallizable oil. The crystals melt at about 76° and are identical with those described and analyzed by Remsen and Dohme.[1] It was, further, made

[1] This Journal, 11, 341.

extremely probable that the solid chloride is the symmetrical one of the formula $C_6H_4<^{COCl}_{SO_2Cl}$, and that the lower-melting chloride is the unsymmetrical one of the formula $C_6H_4<^{CCl_2}_{SO_2}>O$. According to this, one of the anilides is to be represented by the formula $C_6H_4<^{CONHC_6H_5}_{SO_2NHC_6H_5}$ and the other by $C_6H_4<^{C(NHC_6H_5)_2}_{SO_2}>O$.

Still later, A. P. Saunders and myself succeeded in obtaining both the chlorides in crystallized condition and showed that the lower-melting one melts, in fact, at 21.5°–22.5°. We found that both of the chlorides give ordinary orthosulphobenzoic acid when treated with water; that the symmetrical chloride gives benzoic sulphinide, $C_6H_4<^{CO}_{SO_2}>NH$, with ammonia,

$$C_6H_4<^{COCl}_{SO_2Cl}+4NH_3=C_6H_4<^{CO}_{SO_2}>N.NH_4+2NH_4Cl,$$

and A. D. Chambers, working in this laboratory, has recently found that the lower-melting or unsymmetrical chloride reacts with ammonia to form the ammonium salt of orthocyanbenzenesulphonic acid, thus,

$$C_6H_4<^{CCl_2}_{SO_2}>O+4NH_3=C_6H_4<^{CN}_{SO_2NH_4}+2NH_4Cl.$$

At the same time some benzoic sulphinide is formed, probably in consequence of a partial transformation of the unsymmetrical into the symmetrical compound. Ammonia acts upon the unsymmetrical chloride much more readily than upon the symmetrical, and upon this fact is based a method, devised by J. E. Bucher, in this laboratory, for the preparation of the symmetrical chloride in pure condition. Other reagents, as water and caustic alkalies, also act first upon the unsymmetrical chloride.

When the mixed chlorides act on benzene and aluminium chloride, a product is first formed which is, apparently, orthobenzoylbenzenesulphone chloride, $C_6H_4<^{CO.C_6H_5}_{SO_2Cl}$. The

same product is obtained when the pure symmetrical chloride is used. By continued action of benzene and aluminium chloride on the chlorides or on the above-mentioned intermediate product, orthobenzoyldiphenylsulphone, $C_6H_4<^{COC_6H_5}_{SO_2C_6H_5}$ is obtained. This compound breaks down under the influence of fusing potassium hydroxide, yielding diphenylsulphone and benzoic acid:

$$C_6H_4<^{COC_6H_5}_{SO_2C_6H_5} + KOH = C_6H_5.SO_2.C_6H_5 + C_6H_5.COOK.$$

The action of phenols upon the chlorides is peculiar and will require further study. Thus far it can only be said that both chlorides, apparently, have a tendency to go over finally to a colored substance like phenolphthalein, but yield crystallized products if the reaction is checked after a few moments. In this way from the mixed chlorides and from the pure solid chloride the normal phenyl ether of orthosulphobenzoic acid, $C_6H_4<^{COOC_6H_5}_{SO_2OC_6H_5}$, is obtained.

The experimental details are communicated in the following articles.

I. THE ACTION OF ANILINE AND OF THE TOLUIDINES ON ORTHOSULPHOBENZOIC ACID AND ITS CHLORIDE.

By Ira Remsen and C. E. Coates, Jr.

An attempt was first made to make the anilide and toluides by heating the aniline and toluidine salts. As these have not previously been prepared brief descriptions of them are first given:

Neutral aniline salt of o-sulphobenzoic acid, $C_6H_4<^{COOH(NH_2C_6H_5)}_{SO_3OH(NH_2C_6H_5)}$.—On adding aniline to a fairly concentrated aqueous solution of the acid, a white voluminous precipitate is thrown down. This precipitate is soluble in alcohol and in considerable hot water. From the solution in hot water, good crystals are readily obtained. They are best obtained pure as follows: Two parts of aniline are added to one part of the acid (in molecular quantities) in aqueous solu-

tion. A small quantity of aniline is then added to ensure excess. The solution is boiled a short time with animal charcoal and filtered while hot. On cooling, transparent crystals separate out, colorless or nearly so, but slowly becoming colored, on standing, in aqueous solution in the light. These crystals are in the form of thick needles or prisms, melt at 165°, and begin to decompose at 185°.

They were analyzed and gave the following results:

I. 0.2605 gram substance gave 0.1606 gram $BaSO_4$.

II and III. Nitrogen determinations (Kjeldahl).

IV. 0.2300 gram substance gave 0.4961 gram CO_2 and 0.1083 gram H_2O.

Calculated for $C_6H_4<^{COOH(NH_2C_6H_5)}_{SO_3OH(NH_2C_6H_5)}$.		Found.
C	58.76	58.82
H	5.15	5.23
N	7.22	7.28–7.18
S	8.25	8.46

As the aqueous solution of the pure salt changed color on boiling in the air, and as, after boiling some time and crystallizing, the melting-point was altered materially, it was surmised that the salt decomposed on boiling, in part, and the base was carried away in the water-vapor, in which the odor of aniline was distinctly noticed. This was found to be the case and, after boiling several hours, decolorizing with animal charcoal, and allowing the concentrated solution to stand over sulphuric acid, white needles were obtained, which, at 108°, melted partially and gave off water. These needles change color on standing in the air, and on analysis proved to be the acid salt.

Calculated for $C_6H_4<^{COOH}_{SO_3OH(NH_2C_6H_5)}+H_2O$.		Found.
H_2O	5.75	5.72
N (in dehydrated salt)	4.75	4.71

All the water is given off below 112°. This salt could be obtained readily by adding aniline to the acid, molecule for molecule by weight, and crystallizing from water. It is very soluble in water and as, on boiling the solution, aniline can still be smelt, the second molecule of aniline is probably also carried away slowly in the steam.

The neutral and acid salts of ortho-, meta-, and para-toluidine were prepared in a manner precisely similar to that employed in the case of aniline.

Neutral p-toluidine salt, $C_6H_4<\begin{matrix}COOH(NH_2C_6H_4CH_3)\\SO_3OH(NH_2C_6H_4CH_3)\end{matrix}$, is soluble in hot water and quite difficultly soluble in cold. It forms large thick needles, colorless when pure, but usually straw-colored. Melting-point, 197°.

I. 0.2126 gram substance gave 0.1223 gram $BaSO_4$.

II and III. Nitrogen determinations.

	Calculated for $C_6H_4<\begin{matrix}COOH(NH_2C_6H_4CH_3)\\SO_3OH(NH_2C_6H_4CH_3)\end{matrix}$.	Found. I.	II.	III.
S	7.69	7.89	....	....
N	6.73	....	6.61	6.54

Acid p-toluidine salt, $C_6H_4<\begin{matrix}COOH\\SO_3OH(NH_2C_6H_4CH_3)\end{matrix}+H_2O$.

—This salt was made by boiling the neutral salt in aqueous solution for some time, or better, by adding molecular weights of *p*-toluidine and the acid in aqueous solution. It consists of colorless needles which lose one molecule of water of crystallization at 100°–110°. It is very soluble in water.

I. 0.7176 gram of substance lost at 110° 0.0391 gram H_2O.

II. 0.7924 gram of substance lost at 110° 0.0436 gram H_2O.

III. Nitrogen determined by Kjeldahl's method.

	Calculated for $C_6H_4<\begin{matrix}COOH\\SO_3OH(NH_2C_6H_4CH_3)\end{matrix}+H_2O$.	Found. I.	II.	III.
H_2O	5.51	5.46	5.50	....
N (in dehydrated salt)	4.53	....	....	4.72

Neutral m-toluidine salt, $C_6H_4<\begin{matrix}COOH(NH_2C_6H_4CH_3)\\SO_3OH(NH_2C_6H_4CH_3)\end{matrix}$, crystallizes in small granular crystals, white, but soon turning pink on exposure to air and light; melting-point, 163.5°.

I. 0.2185 gram substance gave 0.1202 gram $BaSO_4$.

II. Nitrogen determination.

	Calculated for $C_6H_4<\begin{matrix}COOH(NH_2C_6H_4CH_3)\\SO_3OH(NH_2C_6H_4CH_3)\end{matrix}$.	Found.
S	7.69	7.55
N	6.73	6.67

Acid m-toluidine salt, $C_6H_4<\begin{matrix}COOH\\SO_3OH(C_6H_4CH_3NH_2)\end{matrix}+\frac{1}{2}H_2O$.

—Large rhombic crystals, very soluble in water; colorless,

but turning red easily. At 110° it melts nearly completely, at 130° gives off bubbles, and at slightly higher temperature solidifies, melting completely at 164°.

0.0374 gram of acid *m*-salt lost at 104° 0.0156 gram H_2O.

	Calculated for $C_6H_4<\begin{matrix}COOH\\SO_2OH(C_6H_4CH_3NH_2)\end{matrix}+\frac{1}{2}H_2O$.	Found.
H_2O	2.83	2.9
N (in dehydrated salt)	4.53	4.54–4.41

Neutral o-toluidine salt, $C_6H_4<\begin{matrix}COOH(NH_2C_6H_4CH_3)\\SO_2OH(NH_2C_6H_4CH_3)\end{matrix}$

—White needles, turning pinkish. Quite soluble in water. Easily decomposed by boiling, forming the acid salt very readily and giving off *o*-toluidine. Melting-point of crystals 127.5°.

0.2172 gram substance gave 0.1196 gram $BaSO_4$.

	Calculated for $C_6H_4<\begin{matrix}COOH(C_6H_4CH_3NH_2)\\SO_2OH(C_6H_4CH_3NH_2)\end{matrix}$.	Found.
N	6.73	6.67
S	7.69	7.56

Acid o-toluidine salt, $C_6H_4<\begin{matrix}COOH\\SO_2OH(NH_2C_6H_4CH_3)\end{matrix}+\frac{1}{2}H_2O$.

—Crystallizes in white needles, very soluble in water and in alcohol.

I. 0.7280 gram substance lost 0.0209 gram H_2O.

II. 0.6803 gram substance lost 0.0197 gram H_2O.

III. Nitrogen determination.

	Calculated for $C_6H_4<\begin{matrix}COOH\\SO_2OH(NH_2C_6H_4CH_3)\end{matrix}+\frac{1}{2}H_2O$.	Found. I.	Found. II.	Found. III.
H_2O	2.83	2.87	2.89	...
N (in dehydrated salt)	4.53	...	...	4.4

Having thus obtained the salts of aniline and the toluidines, an attempt was made to obtain the anil and the anilide from the aniline salt by distillation. The aniline salt was heated carefully in a test-tube, but, although at about 185°–190° a change took place, the only result of higher heating was the production of a carbonized mass from which nothing definite could be extracted. Presuming that the anil could not be distilled, the operation was next carried on thus: About a gram of the salt was placed in a very small retort, so constructed that the substances given off could be collected

and the residue weighed. After heating at 195°–205° for several hours and weighing at intervals, it was found that a continual loss in weight took place, amounting at the last weighing to about 32 per cent., and a colorless liquor distilled over, which proved, on investigation, to be aniline. Now, if the following reaction should take place, thus,

$$C_6H_4\begin{matrix}/CO.OH.NH_2C_6H_5\\ \backslash SO_2.OH.NH_2C_6H_5\end{matrix}=C_6H_4\begin{matrix}/CO\\ \backslash SO_2\end{matrix}\rangle N.C_6H_5+NH_2.C_6H_4+H_2O.$$

the loss in weight in consequence of the splitting off of aniline and water would amount to 33.25 per cent. On investigating the residue, however, it proved to be a non-crystalline mass which dissolved in considerable hot water to form a red solution, and which could not be obtained except in a gummy state. It was not decomposed by dissolving in sodium hydroxide.

The para-toluidine salt was treated similarly. At 197° it melted, giving off bubbles of something which proved to be para-toluidine. Heated for several hours at 260°–270°, a point was reached at which the reaction seemed complete. The product was, as before, a gum. It melted at about 95°; was soluble in alcohol and in hot water. In ether it was insoluble. On cooling the hot-water solution, it became turbid and an oil separated out—the same thing which had been dissolved, apparently. It appeared not to be capable of distillation at ordinary pressure. Hence a quantity of the gum was placed in a small retort and distilled at a pressure of 15 mm. As before, carbonization took place to a very great extent, but a small quantity of a substance insoluble in water did pass over.

The ortho-toluidine salt behaved in the same way, though it was not distilled at a reduced pressure. A gum always was obtained which, while apparently a definite substance, could not be obtained in crystalline form. This reaction has not as yet been satisfactorily explained, for while the amount lost by the salt corresponds roughly with the theoretical loss in the formation of the anil or the tolil respectively, the anil and the tolil are both substances with very different properties, as will be shown later.

Action of Aniline on the Chloride of Orthosulphobenzoic Acid.

On adding an excess of aniline to some of the chloride in a little water, violent reaction, with heat, ensued. After heating on the water-bath an hour or so, and adding water, an insoluble substance separated out. Filtered off, it dissolved in alcohol, from which it crystallized in white needles melting from 154°–162°. While it is not absolutely insoluble in hot water, water precipitates it in the cold from concentrated alcoholic solution nearly completely. The same substance was obtained by adding the chloride gradually to an emulsion of aniline in water, keeping cool, and shaking. It is soluble in ether, in alcohol, and in alkalies. Next, the chloride, free from water, was added to aniline, the latter being in excess. After the reaction was over the substance was boiled with water and with hydrochloric acid to remove any excess of aniline. The insoluble residue was crystallized from alcohol after decolorizing with animal charcoal. The crystals were granular, decomposed slowly at temperatures above 250°, were soluble in hot alcohol, and insoluble in water, benzene, and ether.

Fusible Anilide.—After purification, the substance which melted before at 154°–162° was found to melt at 196° fairly sharply. The crystals were as before, thin white needles. These, on *standing* in contact with the alcoholic solution for some time, change slowly over to large, flat crystals, prismatic, some single, some arranged in radiating clusters. On picking them out mechanically and recrystallizing them, they came down again as needles, and again went over slowly to the prismatic form. This latter form resembles closely the crystals of the infusible substance, but the latter are always terminated, apparently, by basal planes, the former always by obtuse pyramids. This similarity of crystal-form led for some time to the conclusion that the substance was not pure, until, trying the melting-point of the prisms, it was found to be identical with that of the needles. Preliminary analyses for sulphur and nitrogen led to the conclusion that the anilide of orthosulphobenzoic acid had been obtained.

It was then attempted to make it in quantity, but though the conditions were varied in many ways, the yields were uni-

formly poor, never over 5 to 10 per cent. of the theoretical. The best results were obtained as follows:

To an emulsion of an excess of aniline in considerable cold water, the chloride was added slowly, shaking occasionally. The vessel was allowed to stand over night, the supernatant liquid poured off, the residue boiled a few minutes with dilute hydrochloric acid to remove aniline, dissolved in dilute sodium hydroxide in slight excess, filtered, and, when cold, the fairly concentrated solution acidified with hydrochloric acid. The flocculent white precipitate was filtered off, dissolved in alcohol, purified by animal charcoal, and crystallized from hot alcohol. It is not very soluble in cold alcohol, but dissolves on heating. Together with the needles there is frequently formed some of the infusible substance. They can be separated by boiling with ether, which dissolves only the former, or by crystallizing from concentrated solution and decanting the light needles from the heavier prisms which sink to the bottom. The melting-point was not absolutely sharp, but, after two crystallizations, there was only a slight softening below 196°.

I. 0.4254 gram substance gave 0.2856 gram $BaSO_4$.

II. 0.2131 gram substance gave 0.1422 gram $BaSO_4$.

III. 0.2000 gram substance gave 0.1358 gram $BaSO_4$.

IV and V. Nitrogen determinations.

VI. 0.2136 gram substance gave 0.0939 gram H_2O and 0.5165 gram CO_2.

VII. 0.2152 gram substance gave 0.0952 gram H_2O and 0.5176 gram CO_2.

Of the portions of substance employed, I, IV, and V were prepared at one time; II, III, and VI at another, and VII at still another.

	Calculated for $C_6H_4<^{CO.NHC_6H_5}_{SO_2NHC_6H_5}$	Found. I.	II.	III.	IV.	V.	VI.	VII.
C	64.77	..	..	..	..	..	65.49	65.59
H	4.55	..	..	..	..	..	4.88	4.92
S	9.09	9.22	9.16	9.32	..	..	..	..
N	7.95	..	..	..	7.98	7.79	..	..

Infusible Anilide.—Attention was now turned to the infusible substance. It was noticed that when several crystals were

heated at 110° a short time to dry them, they lost their transparency and grew chalky. This led to the suspicion that they contained alcohol of crystallization, which proved to be the case. A portion heated at 130° till the weight was constant, was analyzed and found to give, for sulphur and nitrogen, the same figures as the needles had given. A quantity was therefore made in the following manner:

A weighed quantity of aniline was placed in a large, dry test-tube. To this was added, slowly, keeping cool and shaking, such a quantity of the chloride that there should be slightly more than two molecules of aniline for each molecule of the chloride. A violent reaction ensued immediately, and bubbles of hydrochloric acid were given off. In a few minutes the reaction ceased, and the semi-solid mass was heated carefully. More hydrochloric acid was given off. The heating was continued till no more bubbles came off, care being taken not to let the mass get too hot, as then decomposition sets in. The mass was poured on cold porcelain or glass while still fluid, dissolved in alcohol, boiled with animal charcoal, filtered, and crystallized from hot alcohol. The first crystals consisted usually of some needles. These were filtered off. On evaporating the filtrate to a fairly small volume, crystals of the infusible substance were obtained. These were dissolved in hot dilute sodium hydroxide, filtered, and, when cold, precipitated by hydrochloric acid, and the precipitate recrystallized from hot alcohol. The crystals are apparently orthorhombic—though no angles were measured—are always terminated by basal planes, and can be obtained readily, apparently pure, by recrystallizing twice from alcohol. Heated, they lose something at about 160° and turn chalky. At 250° they begin to turn brown. At 270° they begin to melt, with decomposition, and they melt completely to a red liquid at 280°.

About a gram of the crystals was then heated in a large bent tube in a sulphuric-acid bath at 160°. Alcohol was given off, which collected in the cool part of the tube and was recognized both by its smell and by the iodoform reaction.

I. 0.4745 gram substance loses at 130° 0.0553 gram alcohol.

II. 0.5770 gram substance loses at 130° 0.0666 gram alcohol.

In $C_6H_4<^{CONHC_6H_5}_{SO_2NHC_6H_5} + C_2H_5OH$.	Found.	
Calculated for 1 mol. C_2H_5OH.	I.	II.
11.56	11.65	11.54

It was necessary to heat to 130° six or eight hours before a constant weight was obtained. At 150° the alcohol was given off more rapidly, but the substance began to turn slightly dark, so the lower temperature was used. The substance from which the alcohol had been driven off was taken for analysis.

I. 0.2706 gram substance gave 0.1811 gram $BaSO_4$.

II. 0.2510 gram substance gave 0.1698 gram $BaSO_4$.

III and IV. Nitrogen determinations (Kjeldahl).

V. 0.2179 gram substance gave 0.0846 gram H_2O and 0.522 gram CO_2.

VI. 0.2994 gram substance gave 0.126 gram H_2O and 0.7141 gram CO_2.

	Calculated for $C_6H_4<^{CONHC_6H_5}_{SO_2NHC_6H_5}$.	Found. I.	II.	III.	IV.	V.	VI.
C	64.77	...	...	...	...	65.3	65.05
H	4.55	...	...	...	...	4.31	4.67
S	9.09	9.19	9.24	...	...	...	...
N	7.95	...	...	8.04	7.89	...	...

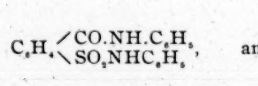
This substance is formed in greater or less quantity whenever aniline and the chloride are heated together. The needles of the fusible anilide appear to be formed only at low temperatures. What the relation between the two anilides is has not as yet been determined definitely. They both dissolve in alkalies and alkaline carbonates; they are reprecipitated by acids; neither one appears to be a strong enough acid to form a salt when boiled with powdered calcite. In short, they have the same general chemical behavior, while they differ markedly in physical properties, though analysis points to an identity of composition. It is probable that there are two chlorides differing from each other thus:

I. $C_6H_4<^{COCl}_{SO_2Cl}$.

II. $C_6H_4<^{Cl\ Cl}_{SO_2}>C<O$.

While of these two formulas, I is usually assigned to the ordinary chloride of orthosulphobenzoic acid, formula II has never been definitely disproved. As is well known, the best

work on the chlorides of succinic and phthalic acids seems to show that in their cases a substance analogous to II must be present as a component of a mixture, if indeed II be not the only proper formula. If this were the case with the chloride of orthosulphobenzoic acid, it is obvious that isomeric anilides could be formed of the formulas



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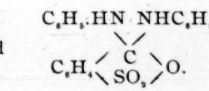


Anil of Orthosulphobenzoic Acid.—In speaking of the infusible anilide, mention was made of some needles which were formed with it and crystallized out first. These were purified and found to melt sharply at 190.5°, and to be insoluble in water, sodium hydroxide, or carbonate. After many experiments the following was decided on as being the best method of preparation:

To a weighed portion of the chloride in a large test-tube, aniline was added in such proportion that there should be slightly more than one molecule of chloride to each molecule of aniline. The proportion should be weighed carefully, as by changing them the products of the reaction are changed also. For example, to 10 grams of chloride add 3½ grams of aniline (theoretical amount required is 3.9 grams). The aniline should be added slowly, and the contents of the test-tube shaken constantly. Violent reaction sets in and subsides in a few moments. Heat carefully over a free flame till no more bubbles of hydrochloric acid are given off, or, perhaps better, heat to the requisite temperature in a sulphuric-acid bath, stirring, and hold at that temperature about half an hour. While still fluid pour out on a piece of cold porcelain. Wash out the test-tube with hot alcohol, dissolve the whole in hot alcohol, boil with animal charcoal, filter, and crystallize. The crystals are long, white flat blades or needles that melt sharply at 190.5°. They are insoluble in water, soluble in hot alcohol, quite difficultly soluble in cold, soluble in hot ether, and difficultly soluble in hot chloroform. They are insoluble in alkalies, but on boiling for some time with dilute sodium hydroxide, they dissolve to a colorless solution,

from which, on acidifying, a new substance is precipitated.

I. 0.209 gram substance gave 0.189 gram $BaSO_4$.

II. 0.2542 gram substance gave 0.2273 gram $BaSO_4$.

III and IV. Nitrogen determinations (Kjeldahl).

V. 0.2196 gram substance gave 0.4865 gram CO_2 and 0.0771 H_2O.

VI. 0.1736 gram substance gave 0.3891 gram CO_2 and 0.0607 H_2O.

	Calculated for $C_6H_4<^{CO}_{SO_2}>NC_6H_5$.	Found. I.	II.	III.	IV.	V.	VI.
C	60.23	....	....	....	....	60.42	61.08
H	3.47	....	....	....	....	3.90	3.88
S	12.36	12.41	12.28	....	....	....	....
N	5.41	....	....	5.61	5.60	....	....

These results show that the substance is the anil,

$$C_6H_4\begin{matrix}/CO\backslash\\\backslash SO_2/\end{matrix}N.C_6H_5.$$

As stated, it was found to be insoluble in alkali. It was noticed, however, that on continued boiling with dilute alkali, a precipitate was obtained on acidifying the filtrate. About a gram of the anil was therefore boiled for an hour with dilute sodium hydroxide and found to dissolve completely. The solution was evaporated to a small volume, and acidified with hydrochloric acid while still hot. A colorless oil separated out, which quickly changed to white, granular crystals. These were soluble in considerable hot water, in alkalies, and alkaline carbonates, and very soluble in alcohol. Acids reprecipitated them from alkaline solution. Analysis gave the following results:

0.1760 gram substance gave 0.1468 gram $BaSO_4$.

	Calculated for $C_6H_4<^{COOH}_{SO_2NHC_6H_5}$.	Found.
S	11.55	11.45

It is therefore, as was expected, the anilic acid, formed from the anil by its taking up a molecule of water:

$$C_6H_4\begin{matrix}/CO\backslash\\\backslash SO_2/\end{matrix}NC_6H_5 + H_2O = C_6H_4\begin{matrix}/COOH\\\backslash SO_2NHC_6H_5.\end{matrix}$$

Of course the facts stated do not prove that the aniline residue is in combination with the sulphone group, SO_2, though

the fact that the acid is not easily soluble in water makes the above view of its constitution probable.

Barium salt of anilic acid, $\left(C_6H_4\begin{smallmatrix}COO\\SO_2NHC_6H_5\end{smallmatrix}\right)_2Ba + Aq$. —The salt was prepared in the usual way, when an oily mass was obtained, but no good crystals; though on drying at 110° in an air-bath this mass changed to small needles, which appeared to give off water of crystallization, and turned eventually to a white powder. They were soluble in alcohol and in water.

0.1282 gram anhydrous salt gave 0.0432 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}COO\\SO_2.NH.C_6H_5\end{smallmatrix}\right)_2Ba$.	Found.
Ba	19.88	19.83

On treating the salt with hydrochloric acid, the anilic acid was reprecipitated unchanged. As it evidently had been formed from the anil by hydrolysis some of the acid thus precipitated was heated in a tube in a sulphuric-acid bath. It melted with slight decomposition at about 173°. Heated to over 200° it lost water, which collected in the top of the tube, and was changed to the anil with further slight decomposition. The anil was crystallized out, found to melt at 190.5°, and to correspond in physical properties exactly with the anil from which the anilic acid had been made originally. The circuit from the anil to anilic acid, to barium salt, to anilic acid, and back to anil, was thus completed.

In making the anil and the two anilides, the mother-liquors frequently contained a large amount of a gummy substance. This was soluble in sodium hydroxide, was precipitated by hydrochloric acid, and was nearly insoluble in cold water. It was very soluble in alcohol, but could not be obtained crystalline from any solvent tried. On boiling with strong hydrochloric acid, however, for some time, the gum grew brittle and, finally, quite hard. From this, by crystallization from alcohol, the anil was obtained, melting at 190.5°.

Experiments, similar to those already described, were carried out with para-, meta-, and ortho-toluidines.

Orthosulphobenzo-para-tolil, $C_6H_4\begin{smallmatrix}CO\\SO_2\end{smallmatrix}>N.C_6H_4CH_3$. —The

tolil was made precisely as the anil. The yield was better than in the case of the anil, but still not more than 30 per cent. of the theoretical at the best, and usually much less. The crystals consisted of bunches of fine needles, perfectly white, and melting sharply at 195.5°. They are insoluble in water, soluble in hot alcohol, soluble in hot ether, and insoluble in alkalies, by which, however, they are decomposed on continued boiling. They are very difficultly soluble in cold alcohol. They behave in all respects like the corresponding aniline compound.

I. 0.2214 gram substance gave 0.1883 gram $BaSO_4$.

II. 0.2017 gram substance gave 0.1746 gram $BaSO_4$.

III and IV. Nitrogen determinations (Kjeldahl).

V. 0.2453 gram substance gave 0.5857 gram CO_2 and 0.0952 gram H_2O.

VI. 0.1906 gram substance gave 0.4346 gram CO_2 and 0.0766 gram H_2O.

	Calculated for $C_6H_4<^{CO}_{SO_2}>N.C_6H_4.CH_3$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	61.54	...	...	...	...	61.77	62.18
H	4.03	...	...	...	...	4.31	4.46
S	11.72	11.76	11.88	...	...	...	...
N	5.13	...	...	5.15	5.32	...	...

A quantity of the tolil was decomposed by continued boiling with dilute sodium hydroxide. The acid was precipitated by hydrochloric acid, and found closely to resemble the anilic acid in appearance. It is not as soluble in water as the latter, but is easily soluble in alkalies and in alcohol. The barium salt could not be obtained in good crystals, but separated as an oily substance from concentrated solutions. Some of this was dried in the air and between layers of filter-paper.

0.1913 gram of the acid, dried at 110°, gave 0.1531 gram $BaSO_4$.

	Calculated for $C_6H_4<^{COOH}_{SO_2NHC_6H_4CH_3}$	Found.
S	11.00	10.99

0.1834 gram of air-dried Ba salt lost, on heating at 110°, 0.0128 gram H_2O.

	Calculated for $(C_6H_4<^{COO}_{SO_2NH.C_6H_4CH_3})_2Ba+3H_2O$.	Found.
H_2O	7.06	6.98

0.1706 gram dehydrated Ba salt gave 0.0557 gram $BaSO_4$.

	Calculated for $Ba.2(C_6H_4<^{COO}_{SO_2NHC_6H_4CH_3})$.	Found.
Ba	19.11	19.21

The salt is decomposed by hydrochloric acid, and the acid itself behaves like the anilic acid, *i. e.*, heated, it melts at about 155° with slight decomposition, and loses water at higher temperatures A portion of the acid was recovered by treating the barium salt with hydrochloric acid. This was dried and heated in a small test-tube till all the water seemed to have been given off. On recrystallizing a couple of times from alcohol the tolil was recovered pure, melting sharply at 195.5°. Thus in the case of the tolil as well as the anil the circuit was made of taking up water, forming the barium salt, decomposing the barium salt and, by splitting off water, regaining the original substance. In speaking of the attempt to make the tolil by distilling the *p*-toluidine salt under diminished pressure, it was mentioned that a small quantity of substance distilled over in spite of the carbonization. This was preserved, and on recrystallizing it from alcohol it was found to give crystals identical in appearance and in melting-point with the tolil just described. The inference is fair, then, that the tolil is formed by distilling the salt, just as succinanil,

$$C_6H_4<^{COOH.NH_2C_6H_4CH_3}_{SO_2OHNH_2C_6H_4CH_3} = C_6H_4<^{CO}_{SO_2}>NC_6H_4CH_3+NH_2C_6H_4CH_3+H_2O,$$

but at the temperature necessary for distillation, carbonization takes place to a great extent, probably because of the presence of sulphuric acid residue.

Orthosulphobenzotoluide, (*para*), $C_6H_4<^{CONHC_6H_4CH_3}_{SO_2NHC_6H_4CH_3}$ (?).

—This was made by adding to the chloride a little more than

twice the molecular quantity of *p*-toluidine, just as in the case of the anilide. The operation was carried on in exactly the same manner as in that instance. The para-toluide crystallizes out of alcoholic solution in transparent cubes, insoluble in ether, soluble in alkalies, from which they are precipitated by acids, nearly insoluble in hot water, and insoluble in cold water. They contain no alcohol of crystallization, and remain unchanged at 250°. They decompose at higher temperatures.

I. 0.3141 gram substance gave 0.1937 gram $BaSO_4$.

II and III. Nitrogen determinations (Kjeldahl).

IV. 0.9233 gram substance gave 2.2274 grams CO_2 and 0.4491 gram H_2O. [In this case the combustion was carried on rather more rapidly than usual.]

V. 0.4108 gram substance gave 0.9995 gram CO_2 and 0.2023 gram H_2O.

	Calculated for $C_6H_4<^{CO.NH.C_6H_4CH_3}_{SO_2NHC_6H_4CH_3}$.	Found. I.	II.	III.	IV.	V.
C	66.32	...	...	...	65.80	66.35
H	5.27	...	...	...	5.39	5.47
S	8.42	8.47	...	...	...	...
N	7.37	...	7.18	7.30	...	...

An attempt was made to make a toluide analogous to the fusible anilide. Para-toluidine in excess was added to an emulsion of the chloride in cold water and allowed to stand for some time, the tube being shaken occasionally. It was then boiled, the insoluble residue dissolved in sodium hydroxide, filtered, and precipitated by hydrochloric acid. The precipitate was dissolved in alcohol, and gave, on standing, two kinds of crystals, the cubes just described and needles melting at about 196°. These needles were obtained only in small quantity, and the experiment was not repeated owing to lack of time. They change, on standing in their mother-liquor, to thick prismatic crystals (as the anilide does). As they are quite soluble in chloroform, while the cubes are insoluble, they can be isolated by boiling the two kinds of crystals with chloroform and filtering off the undissolved cubes. When the chloroform was distilled off and the substance crystallized from alcohol, fine prismatic crystals were found. As it resem-

bles the fusible anilide both as to method of formation and its physical properties, that is, in melting without decomposition, being soluble in alkalies and reprecipitated by acids, and being soluble in chloroform and ether—presumably it is the analogous *p*-toluidine compound.

Orthosulphobenzotolil (*meta*), $C_6H_4\begin{<}{CO \atop SO_2}\end{>}N.C_6H_4CH_3$.—This was made in the same way as the anil and the para-tolil. It crystallizes in colorless needles which melt sharply at 147.5°. By crystallizing slowly from alcohol it can be obtained in grains and prisms. Its physical properties are similar to those of the anil and *p*-tolil.

I. 0.1959 gram substance gave 0.1725 gram $BaSO_4$.

II. 0.2609 gram substance gave 0.5920 gram CO_2 and 0.1026 gram H_2O.

III. 0.2184 gram substance gave 0.5001 gram CO_2 and 0.0859 gram H_2O.

	Calculated for $C_6H_4\begin{<}{CO \atop SO_2}\end{>}NC_6H_4.CH_3$.	Found. I.	II.	III.
C	61.54	...	61.88	61.53
H	4.03	...	4.36	4.37
S	11.72	12.08	...	...

Orthosulphobenzotoluide (*meta*), $C_6H_4\begin{<}{CONHC_6H_4CH_3 \atop SO_2NHC_6H_4CH_3}\end{>}+C_2H_5OH$.—By adding to the chloride slightly more than twice the molecular quantity of meta-toluidine, and carrying out the operation as in the case of the infusible anilide and toluide, the meta-toluide was obtained in short prismatic crystals, not melting at 250°, and with physical properties like those of the infusible anilide. It contains one molecule of alcohol of crystallization, which it loses slowly at 120°. The substance from which the alcohol has been driven off is somewhat hygroscopic.

1.0272 gram substance lost 0.1130 gram of alcohol at 120°.

	$C_6H_4\begin{<}{CO.NHC_6H_4CH_3 \atop SO_2.NHC_6H_4CH_3}\end{>}+C_2H_5OH$.	Found.
C_2H_5OH	10.8 per cent.	11 per cent.

I. 0.2695 gram *m*-toluide without alcohol of crystallization gave 0.1668 gram $BaSO_4$.

II. 0.1703 gram gave 0.4154 gram CO_2 and 0.0867 gram H_2O.

	Calculated for $C_6H_4<^{CO.NHC_6H_4CH_3}_{SO_2.NHC_6H_4CH_3}$.	Found.
C	66.32	66.52
H	5.26	5.60
S	8.42	8.49

As in the case of the anilide, the alcohol of crystallization was driven off, collected, and identified both by its odor and by the iodoform reaction.

The attempt to make the isomeric meta-toluide, analogous to the anilide melting at 195°–196°, was carried out as follows: The chloride was added slowly to an emulsion of an excess of the *m*-toluidine in ice-water, with constant shaking. The mixture was allowed to stand several hours, then washed with hydrochloric acid, and the residue dissolved in sodium hydroxide. It was boiled till most of the smell of *m*-toluidine had disappeared; filtered and precipitated with hydrochloric acid. A gum separated out which was somewhat soluble in water. It dissolved in alcohol very easily. On carefully adding water to the alcoholic solution, a crystalline deposit was obtained. This was filtered off, washed, and dissolved in alcohol, from which it crystallizes well in large grains, melting quite sharply at 161.5°–162.5°. These crystals were soluble in alcohol, ether, and chloroform. From alkaline solution the substance was precipitated, unchanged by acids. It behaved in every way like the anilide melting at 195°–196°, and the substance which was presumably the fusible *p*-toluide. Owing to lack of time only sulphur could be determined.

0.1625 gram substance gave 0.0978 gram $BaSO_4$.

	Calculated for $C_6H_4<^{CO.NHC_6H_4CH_3}_{SO_2NHC_6H_4CH_3}$.	Found.
S	8.42	8.23

It is therefore, in all probability, isomeric with the infusible *m*-toluide. This isomerism can be explained in the same manner as was that of the anilides.

Orthosulphobenzotolil (*ortho*), $C_6H_4<^{CO}_{SO_2}>N.C_6H_4CH_3$.—This was made in the same manner as the anil and the other

tolils. It is more soluble in alcohol than any of them, and was obtained in short, thick needles or plates, melting not very sharply at 172°–175° after several recrystallizations. It had the same general physical properties as the homologous compounds.

I. 0.1982 gram substance gave 0.1657 gram $BaSO_4$.

II. 0.1856 gram substance gave 0.1543 gram $BaSO_4$.

III. 0.3455 gram substance gave 0.7792 gram CO_2 and 0.1278 gram H_2O.

IV. 0.3357 gram substance gave 0.757 gram CO_2 and 0.1273 gram H_2O.

	Calculated for $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NC_6H_4CH_3$.	Found. I.	II.	III.	IV.
C	61.54	....	....	61.51	61.50
H	4.03	....	....	4.11	4.21
S	11.72	11.47	11.42	....	....

Orthosulphobenzotoluide (*ortho*), $C_6H_4\begin{matrix}CO.NH.C_6H_4CH_3\\SO_2NHC_6H_4CH_3\end{matrix}+2C_2H_5OH$(?).—On attempting to make this by following the method used for the other toluides, nothing was at first obtained. It was made, finally, in the following manner: A slight excess of *o*-toluidine was added to the chloride and heated as in the case of the anilide. On crystallizing from alcohol, after boiling with animal charcoal, some crystals of the *o*-tolil (melting-point, 172°–174°) were obtained. These were filtered off, the mother-liquor evaporated to a small volume, and the gummy mass dissolved in a little sodium hydroxide. Some tolil was left undissolved and filtered off. After boiling the sodium-hydroxide solution until no more odor of toluidine was noticed, and acidifying with hydrochloric acid, a considerable quantity of granular crystals separated out on cooling. These were soluble in considerable hot water and easily soluble in alcohol. From the alcoholic solution, water precipitates the substance as a liquid, which gradually becomes crystalline. From *very* concentrated alcoholic solutions prismatic crystals are deposited, resembling in form those of the infusible anilide. On standing even a short time in the air they give off alcohol of crystallization, and

effloresce, turning chalky and crumbling under the touch. On this account the figures for alcohol of crystallization were not close, but there are probably two molecules. The crystals do not melt without decomposition, and they behave like the infusible anilide. The substance from which the alcohol had been driven off (at 120°) gave the following analytical results:

I. 0.3418 gram substance gave 0.2146 gram $BaSO_4$.

II. Nitrogen determination (Kjeldahl).

	Calculated for $C_6H_4<^{CO.NHC_6H_4CH_3}_{SO_3NHC_6H_4CH_3}$.	Found.
S	8.41	8.62
N	7.37	7.34

An estimation of sulphur was made in the crystals precipitated from alkaline solution by acid.

0.2148 gram gave 0.1285 gram $BaSO_4$.

	Calculated.	Found.
S	8.42	8.21

A combustion was made of a small quantity of somewhat impure material, which was all there was at hand. Owing to limited time, a fresh supply of pure substance could not be made.

0.2395 gram substance (impure), from which alcohol of crystallization had been driven off, gave 0.5879 gram CO_2 and 0.1178 gram H_2O.

	Calculated for $C_6H_4<^{CO.NHC_6H_4CH_3}_{SO_3NHC_6H_4CH_3}$.	Found.
C	66.32	66.93
H	5.26	5.46

An attempt was made to prepare the isomeric ortho-toluide corresponding to the fusible anilide and meta-toluide, but nothing definite was obtained owing, possibly, to the fact that the substance was too soluble to crystallize from ethyl alcohol, which was the solvent employed. The same method was employed as in the case of the anilide, *i. e.*, shaking the chloride and the toluidine together in cold water, but only the infusible toluide just described was obtained.

Summary.

1. The aniline and toluidine salts, both acid and neutral, of orthosulphobenzoic acid were made and analyzed.

2. The neutral salt is decomposed on boiling in aqueous solution, giving off the base and forming first the acid salt, and then, possibly, the free acid.

3. While on distillation the salts are, for the most part, carbonized, nevertheless, the para-tolil, at least, is formed in small quantity by distilling the neutral salt at 15 mm. pressure. The neutral salts, moreover, on being heated for some time to about 230°, give off the base in part, and form a gum which may be the unsymmetrical anil or tolil.

4. The anil and the tolils are formed by the action of the chloride on the bases, molecule for molecule.

5. They take up water when boiled with dilute alkalies and form the anilic and tolilic acids, which form, in turn, definite salts, and revert to the anil or tolil respectively when heated above 200°, losing water.

6. The formation of two anilides of markedly different physical properties, and the formation, in the same manner, of two meta-toluides, and probably two para-toluides, tends to confirm the view that the chloride of orthosulphobenzoic acid is a mixture of the two compounds

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} \text{ and } C_6H_4\begin{cases}CCl_2\\SO_2\end{cases}O.$$

II.—FURTHER STUDY OF THE ACTION OF ANILINE ON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

By Ira Remsen and E. P. Kohler.

As the results of the investigation by Remsen and Coates made it appear probable that the chloride of orthosulphobenzoic is a mixture of two isomeric substances, the work was continued in the hope of obtaining further evidence. The chloride was prepared in the usual manner from the pure acid potassium salt of the acid. After heating on the water-bath for some time, the mass was poured into a large quantity of cold water. On separating it from this it was washed with

almost boiling water until neither the last washings nor a solution obtained by decomposing a small quantity of the oil with boiling water gave any reaction for phosphoric acid. Finally, it was dried over concentrated sulphuric acid and solid caustic potash. Thus prepared, the product is a colorless oil which assumes a waxy consistency after standing over sulphuric acid for some time.

Attempts to separate the constituents of the chloride by means of ether, chloroform, and benzine, were not successful. Well-formed needles were obtained together with an oil, but the products were of such a character as to make their investigation unpromising. When the chloride is treated with cold water, it gradually changes to a network of crystals imbedded in an oily matrix. This is the simplest method of obtaining the crystals. A layer of the oil, just thick enough to cover the bottom of the vessel used, is covered with cold water and allowed to stand in a cool place until no further increase in the amount of crystals formed is observed. The water and oil are then rapidly poured off, and the crystals which cling to the bottom of the vessel washed, first with a jet of cold water and, finally, with a little ether.

If the crystals obtained by any of the above methods are dissolved in ether, chloroform, or benzine, they crystallize out again, readily and completely.

Neither the benzine nor the ethereal solution gives any sign of decomposition. The result is the same whether the temperature is kept constant or not, or whether the evaporation is slow or rapid. After one recrystallization the crystals melt sharply at 76° and resolidify on cooling.

These crystals undoubtedly are the substance described by Remsen and Dohme[1] as orthosulphobenzoyl chloride. An analysis gave the following results:

I. 0.2015 gram substance gave 0.2393 gram AgCl.

II. 0.2205 gram substance gave 0.2621 gram AgCl.

	Calculated for $C_7H_4SO_3Cl_2$.	Found. I.	Found. II.
Cl	29.65	29.46	29.4

These facts are given in detail to show that the product of the action of phosphorus pentachloride upon salts of ortho-

[1] This Journal, 11, 332.

sulphobenzoic acid does not act towards solvents like a single individual. The peculiarities observed are most readily explained on the assumption that the product is composed of two compounds, one a solid melting at 76°, the other an oily liquid capable of dissolving the solid. As this view is supported by the chemical behavior of the product, the terms *liquid* and *solid* will hereafter be used to distinguish the two constituents of the mixture, while the term *mixed chlorides*, or simply *chloride*, will be used to designate the entire product.

Behavior of the Chloride on Heating.—An accidental modification of the conditions while preparing some of the chloride showed that it is easily decomposed either by heat or an excess of phosphorus pentachloride. A quantity of acid potassium orthosulphobenzoate was treated with a considerable excess of phosphorus pentachloride, warmed on the water-bath for some time, and then allowed to stand over night. In the morning the chlorides of phosphorus were distilled off as completely as possible at 120°, and the residue washed with cold water. A very decided odor resembling that of benzoyl chloride was observed. When hot water was added to the dark-colored liquid it solidified almost completely, the odor of benzoyl chloride disappearing at the same time. The mass was dissolved in boiling water, filtered in order to remove a small quantity of insoluble tarry matter, boiled with animal charcoal, and allowed to crystallize. The liquid became filled with a mass of yellowish white needles, which, after recrystallization from water, were of a pure white color and melted sharply at 137°. By their melting-point and other physical properties they were easily identified as orthochlorbenzoic acid. This showed that the chlorides of orthosulphobenzoic acid yield a chlorbenzoyl chloride much more readily than the corresponding meta- and para-compounds. As this might affect the purity of the chloride used in subsequent experiments, the conditions under which this decomposition takes place were carefully studied, with the following results:

When heated alone the chloride begins to decompose slowly at 150°. The decomposition increases in rapidity as the temperature is raised until the boiling-point of chlorbenzoyl chlo-

ride is reached. The decomposition is probably represented by the equation

$$C_7H_4SO_2Cl_2 = C_6H_4\begin{cases}Cl\\COCl\end{cases} + SO_2,$$

while secondary reactions give rise to a considerable quantity of tarry material. The decomposition is not affected by the presence of phosphorus oxychloride. Phosphorus pentachloride greatly assists the decomposition, lowering the initial temperature to 100°, and diminishing the amount of resinous material formed. The reaction is probably expressed by the equation

$$C_7H_4SO_2Cl_2 + PCl_5 = C_6H_4\begin{cases}Cl\\COCl\end{cases} + SO_2Cl_2 + PCl_3.$$

In the reaction between phosphorus pentachloride and salts of orthosulphobenzoic acid, a product free from orthochlorbenzoic acid can be readily obtained by avoiding an excess of phosphorus pentachloride and a temperature above 100°.

I. *Action of Aniline on the Mixed Chlorides in the Presence of Water.*—32 grams of aniline were added to 20 grams of the chloride in an emulsion in a liter of water. The mixture was shaken until no more aniline was taken up. The excess of aniline was then distilled off in a current of steam, the liquid removed by filtration, and the insoluble residue dried, powdered, and extracted with boiling ether. The ethereal solution, on evaporation, gave only the substance described by Remsen and Coates as the fusible anilide of orthosulphobenzoic acid.

The residue from the ethereal extract was the infusible anilide of orthosulphobenzoic acid, practically pure. The filtrate from the part insoluble in water was evaporated to a small volume and allowed to cool. A considerable quantity of pure infusible anilide crystallized out. On further evaporation of the mother-liquor a mixture was obtained, which it was impossible to separate by recrystallization. The mother-liquor was therefore evaporated to dryness, the residue powdered and extracted with boiling ether. The ethereal solution contained only aniline hydrochlorate. The residue insoluble in ether gave, on recrystallization from water, a new substance which, as will be shown later, is the aniline salt of orthosulph-

anilidobenzoic acid. The proportion in which the different substances derived from orthosulphobenzoyl chloride were obtained is as follows:

18.7 grams of infusible anilide, corresponding to 64.5 per cent. of the chloride.

6.4 grams of fusible anilide, corresponding to 2.2 per cent. of the chloride.

2.8 grams of the salt, corresponding to 9 per cent. of the chloride.

Not accounted for, 4.5 per cent. of the chloride.

II. *Action of Aniline on the Dry Mixed Chlorides.*—Aniline was slowly added to 20 grams of chloride until a decided odor of aniline remained after the mixture had been warmed on the water-bath for some time. Water was then added to the mass, and the excess of aniline distilled off in a current of steam. The remainder was evaporated to dryness and the residue extracted with ether. The ethereal solution contained only orthosulphobenzanil and a small quantity of aniline hydrochloride. The residue insoluble in ether was extracted with a boiling mixture of alcohol and ether. This solution contained the infusible anilide, which separated out almost completely on cooling, and some aniline hydrochloride which remained in solution. The small portion insoluble in the mixture gave, on recrystallization from water, the aniline salt of sulphanilidobenzoic acid. The relative amounts in which the different substances are formed are as follows:

19.2 grams of infusible anilide, corresponding to 66.2 per cent. chloride.

5.3 grams of anil, corresponding to 24.5 per cent. chloride.

2 grams of salt, corresponding to 6.5 per cent. chloride.

Not accounted for, 3.2 per cent. chloride.

III. *Action of Aniline upon the Pure Solid Chloride in the Presence of Water.*—2 grams of the crystalline chloride were powdered and suspended in water. Aniline was then added until it was no longer acted upon. The reaction was very slow, requiring several days for its completion. The product was treated as in I (page 333). Only the fusible anilide was obtained. The yield was 98 per cent. of the theoretical. This experiment was repeated a number of times, but nothing except the fusible anilide was ever obtained.

IV. *Action of Aniline on the Dry Solid Chloride.*—About 2 grams of the solid chloride were melted on the water-bath and aniline added until it was in slight excess. The product was treated as in II (page 334). Only the anil and aniline hydrochlorate were obtained. This experiment was also performed a number of times with invariably the same results.

V. *Action of Aniline on the Purest Liquid Chloride Obtained.*—Portions of the chloride from which the solid constituent had been removed, as completely as possible, by means of chloroform were treated with aniline as in I and II. The products were the same as those obtained from the mixed chlorides.

The facts established by means of these experiments, as well as those revealed by the study of the behavior of the chloride towards solvents, lead to the conclusion that it is a mixture of two substances, and that the isomerism observed in the anilides, whatever its nature, is to be referred to similar relations between these two chlorides. The experiments show conclusively that the solid chloride gives no infusible anilide, no matter under what conditions aniline is allowed to react with it, and that the infusible anilide is invariably formed when aniline reacts with a chloride which contains some of the liquid material, the amount of infusible anilide formed, increasing in the proportion that the solid chloride is removed from the mixture.

The Anil.—Orthosulphobenzanil, as previously mentioned, is the only derivative of orthosulphobenzoic acid obtained by the action of aniline on the dry solid chloride. The reaction is quantitative, aniline hydrochloride being the other product. It may therefore be expressed by the equation

$$C_6H_4\begin{<}\begin{matrix}COCl\\SO_2Cl\end{matrix}+3C_6H_5NH_2=C_6H_4\begin{<}\begin{matrix}CO\\SO_2\end{matrix}\begin{>}N.C_6H_5+2C_6H_5NH_2Cl.$$

It has been shown that the anil is formed in small quantities by the action of dry aniline upon the mixed chlorides, and it will be shown later that it is also formed by the action of phosphorus pentachloride upon orthosulphanilidobenzoic acid.

The general properties of the anil have been described by

Remsen and Coates. It is difficult to get it in an absolutely pure condition. When recrystallized from alcohol it invariably softens slightly at 180°–185°, and then melts completely at 190°. The best results were obtained by recrystallizing it from a mixture of alcohol and ether. A specimen prepared in this way gave, on analysis, the following results :

I. 0.2103 gram substance gave 0.4633 gram CO_2 and 0.0760 gram H_2O.

II. 0.2181 gram substance gave 0.4809 gram CO_2 and 0.0725 gram H_2O.

III. 0.1085 gram substance gave 0.0988 gram $BaSO_4$.

IV. 0.1562 gram substance gave 0.1403 gram $BaSO_4$.

	Calculated for $C_6H_4<^{CO}_{SO_2}>N.C_6H_5$.	Found. I.	II.	III.	IV.	V.	VI.
C	60.23	60.08	60.13	...	...	...	...
H	3.47	4.02	3.69	...	...	...	...
S	12.36	...	...	12.41	12.51	...	...
N	5.41	...	...	...	...	5.36	5.32

In its chemical properties the anil closely resembles the mother-substance, benzoic sulphinide. When boiled with dilute hydrochloric acid it gradually goes into solution. On evaporating the solution to a small volume, long, colorless needles are obtained, which, as shown by analysis, consist of the acid aniline salt of orthosulphobenzoic acid, which was obtained by Remsen and Coates by the action of one molecule of aniline upon one molecule of orthosulphobenzoic acid. A determination of the sulphur in the compound gave the following results :

I. 0.2105 gram substance gave 0.1618 gram $BaSO_4$.

II. 0.1420 gram substance gave 0.1108 gram $BaSO_4$.

	Calculated for $C_6H_4<^{COOH}_{SO_3ONH_3.C_6H_5}$.	Found. I.	II.
S	10.52	10.6	10.65

The nature of the substance is also shown by its behavior toward alkalies. When caustic potash solution is added to the solution of the salt, aniline is liberated at once, and if the solution is then strongly acidified with concentrated hydrochloric acid, the acid potassium salt of orthosulphobenzoic acid crystallizes out.

The action of hydrochloric acid upon orthosulphobenzanil is therefore analogous to the action of the same reagent upon benzoic sulphinide:

1. $C_6H_4\begin{cases}CO\\SO_2\end{cases}NH+2H_2O=C_6H_4\begin{cases}COOH\\SO_2ONH_4\end{cases}$

2. $C_6H_4\begin{cases}CO\\SO_2\end{cases}N.C_6H_5+2H_2O=C_6H_4\begin{cases}COOH\\SO_2ONH_3C_6H_5\end{cases}$

The anil is insoluble in cold dilute alkalies, but goes into solution on boiling. From this solution mineral acids precipitate an acid which passes back into the anil on heating. This acid was also prepared by another method, which shows its structure and that of the anil derived from it.

When orthotoluenesulphone chloride is treated with aniline, orthotoluenesulphonanilide is obtained. In this compound the aniline residue must be in combination with sulphur. By oxidation with potassium permanganate it is converted into orthosulphanilidobenzoic acid, thus,

$$C_6H_4\begin{cases}CH_3\\SO_2NHC_6H_5\end{cases}+3O=C_6H_4\begin{cases}COOH\\SO_2NHC_6H_5\end{cases}+H_2O.$$

This acid, in which the aniline must likewise be united with sulphur, was found to be identical with the acid obtained by the action of alkalies upon the anil. On heating, it passes into the anil according to the equation

$$C_6H_4\begin{cases}COOH\\SO_2NHC_6H_5\end{cases}=C_6H_4\begin{cases}CO\\SO_2\end{cases}N.C_6H_5+H_2O.$$

These transformations are analogous to those by which benzoic sulphinide was first obtained by Remsen and Fahlberg[1]:

(1) $C_6H_4\begin{cases}CH_3\\SO_2Cl\end{cases}+2NH_3=C_6H_4\begin{cases}CH_3\\SO_2NH_2\end{cases}+NH_4Cl.$

(2) $C_6H_4\begin{cases}CH_3\\SO_2NH_2\end{cases}+3O=C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}+H_2O.$

(3) $C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}=C_6H_4\begin{cases}CO\\SO_2\end{cases}NH+H_2O.$

The passage from the anilic acid to the anil is, however, by no means as easy as the corresponding passage to the sulphinide. The transformation by heating is not satisfactory, as at the high temperature required other decompositions take place to a considerable extent. With the aid of phosphorus penta-

[1] This Journal, 1, 426.

chloride the passage can be readily and cleanly made at the ordinary temperature. For this purpose the anilic acid is dissolved in dry chloroform, and the calculated amount of phosphorus pentachloride added to the solution. The evolution of hydrochloric acid begins at once and the reaction is complete in a few minutes. By distilling off the chloroform and chlorides of phosphorus as completely as possible under diminished pressure, and crystallizing the residue from a mixture of alcohol and ether, pure orthosulphobenzanil is obtained. It was impossible to obtain an intermediate chlorine-product, although the reaction probably takes place in two stages, as represented by the equations:

(1) $C_6H_4\begin{cases}COOH\\SO_2NH.C_6H_5\end{cases}+PCl_5=C_6H_4\begin{cases}COCl\\SO_2NHC_6H_5\end{cases}+HCl+POCl_3.$

(2) $C_6H_4\begin{cases}COCl\\SO_2NHC_6H_5\end{cases}=C_6H_4\begin{cases}CO\\SO_2\end{cases}NC_6H_5+HCl.$

These reactions leave little doubt that the substance is the symmetrical anil of orthosulphobenzoic acid, and, as it is formed quantitatively from the solid chloride, the natural conclusion is that the latter is the symmetrical dichloride of orthosulphobenzoic acid, represented by the formula

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases}.$$

It has also been shown that the fusible anilide is the only product obtained by the action of aniline upon the solid chloride in the presence of water. This leads to the conclusion that the fusible anilide is the symmetrical dianilide of orthosulphobenzoic acid, a conclusion which, as will be shown later, is confirmed by the chemical properties of the substance.

Reaction of the Anil with Aniline.—The anil readily dissolves in cold aniline. From this solution the anil is obtained unchanged if the aniline is distilled off in a current of steam. If the solution is boiled for a few hours before the aniline is distilled off with steam, the residue, when crystallized from alcohol, gives pure fusible anilide, in calculated quantity. This experiment was repeated a number of times under modified conditions, in order to determine whether the infusible anilide could in any way be formed by the direct addition of aniline

to the symmetrical anil. Nothing but the fusible anilide was ever obtained. The reaction is, doubtless, analogous to that observed by Remsen and Dohme[1] in the case of benzoic sulphinide:

$$C_6H_4\begin{cases}CO\\SO_2\end{cases}NH+C_6H_5NH_2=C_6H_4\begin{cases}CONHC_6H_5\\SO_2NH_2\end{cases}.$$

$$C_6H_4\begin{cases}CO\\SO_2\end{cases}NC_6H_5+C_6H_5NH_2=C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases}.$$

The Fusible Anilide.—This substance is formed quantitatively by the action of aniline upon the solid chloride in the presence of water. It is also formed in small quantity by the action of aniline upon the mixed chlorides in the presence of water, and, in calculated amounts, by the direct addition of aniline to the anil. It is readily obtained in pure form by recrystallization from alcohol or ether. A complete analysis gave the following results:

0.1347 gram substance gave 0.3200 gram CO_2 and 0.0559 gram H_2O.

0.1842 gram substance gave 0.4383 gram CO_2 and 0.0808 gram H_2O.

0.2008 gram substance gave 0.1344 gram $BaSO_4$.

0.2102 gram substance gave 0.1417 gram $BaSO_4$.

	Calculated for $C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases}$.	Found. I.	II.	III.	IV.	V.	VI.
C	64.77	64.77	64.9	...	...	...	...
H	4.55	4.67	4.95	...	...	...	...
S	9.09	...	...	9.22	9.26	...	...
N	7.95	...	...	...	...	7.89	7.86

The chemical behavior of this substance is, throughout, that of an acid anilide. When boiled with dilute hydrochloric acid it gradually goes into solution. From this solution there is obtained, on concentration, first, a mass of highly colored needles, and then a smaller quantity of thin, glistening plates. The needles, on recrystallization from water, are obtained colorless, and, as shown by analysis and comparison, are composed of the acid aniline salt of orthosulphobenzoic acid, which was also obtained by similar treatment of the anil. A

[1] *Loc. cit.*

determination of the sulphur contained in the compound gave the following results:

0.1614 gram substance gave 0.1270 gram $BaSO_4$.

0.1410 gram substance gave 0.1110 gram $BaSO_4$.

	Calculated for $C_6H_4<^{COOH}_{SO_2NH_3C_6H_5}$.	Found. I.	II.
S	10.76	10.8	10.86

The leaflets, on recrystallization from water, melted at 192°, gave off aniline on addition of cold alkali, and were, undoubtedly, aniline hydrochlorate. The decomposition with hydrochloric acid is therefore represented by the equation

$$C_6H_4<^{CONHC_6H_5}_{SO_2NHC_6H_5} + HCl + 2H_2O = C_6H_4<^{COOH}_{SO_2ONH_3C_6H_5} + C_6H_5NH_3Cl.$$

The anilide readily dissolves in dilute alkalies, and crystallizes out again unchanged if this solution is neutralized with dilute acids. If the solution is boiled for a short time and then acidified, the orthosulphanilidobenzoic acid, previously obtained by the action of alkalies on orthosulphobenzanil, and by the oxidation of orthotoluenesulphonanilide, is obtained. It is readily identified by its melting-point and crystal form. Part of the acid is generally decomposed by the alkali, as a small quantity of acid potassium orthosulphobenzoate is also obtained. If a strongly alkaline solution is boiled for a sufficiently long time (six to eight hours were generally found sufficient), the decomposition into the potassium salt of orthosulphobenzoic acid is complete, all the aniline passing off with the steam. With alkalies, therefore, the fusible anilide is decomposed in two stages, as represented by the equations:

(1) $C_6H_4<^{CONHC_6H_5}_{SO_2NHC_6H_5} + KOH = C_6H_4<^{COOK}_{SO_2NHC_6H_5} + NH_2C_6H_5.$

(2) $C_6H_4<^{COOK}_{SO_2NHC_6H_5} + KOH = C_6H_4<^{COOK}_{SO_2OK} + NH_2C_6H_5.$

These decompositions, both with acids and alkalies, are characteristic of acid anilides, while the fact that the decomposition with alkalies takes place in two stages is most readily

explained on the supposition that the two aniline residues bear different relations to the molecule. This leads to the structure $C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases}$, which represents one aniline residue as united with carbon and the other with sulphur. As will be shown later, it is much more difficult to saponify a sulphonanilide than the corresponding carbonic anilide. It is, therefore, to be expected that a dianilide with this structure would, under proper conditions, lose, first the aniline residue combined with carbon, and eventually all the aniline. That this takes place with the fusible anilide follows from the fact that the product obtained in the first stage of the action of alkalies undoubtedly has the aniline combined with sulphur.

Taking all these facts into consideration—the formation from the chloride which, under other conditions, gives only symmetrical orthosulphobenzanil; the ease with which it passes into the same anil by loss of aniline, and is formed from the anil by addition of aniline; the chemical behavior, which is, throughout, that of an acid anilide; and its decomposition into orthosulphobenzoic acid and aniline in two stages—there can be no reasonable doubt that the fusible anilide is the symmetrical dianilide of orthosulphobenzoic acid, as represented by the formula $C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases}$.

The Infusible Anilide.—This substance is invariably the main product of the action of aniline upon the mixed chlorides. The best way to purify it is to recrystallize it from boiling water, from which it is obtained in colorless orthorhombic prisms. An analysis of the substance purified in this way gave the following results:

I. 0.2802 gram substance gave 0.1867 gram $BaSO_4$.

II. 0.2051 gram substance gave 0.1376 gram $BaSO_4$.

III. 0.1231 gram substance gave 0.2933 gram CO_2 and 0.053 gram H_2O.

IV. 0.1300 gram substance gave 0.3097 gram CO_2 and 0.0573 gram H_2O.

	Calculated for $C_{18}H_{14}SO_3N_2$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	64.77	...	...	64.98	64.8	...	...
H	4.57	...	...	4.71	4.91	...	...
S	9.09	9.15	9.22	...	...	...	...
N	7.95	...	...	...	...	7.96	7.89

In its chemical conduct the infusible anilide is characterized by remarkable resistance to the action of most reagents. When boiled with hydrochloric acid of the same strength as that used to transform the fusible anilide and the anil into acid aniline orthosulphobenzoate, it goes into solution, but crystallizes out again unchanged on cooling. The result is the same no matter what the strength of the acid used may be, or at what temperature the two are heated together. In a final experiment the anilide was heated in a sealed tube with concentrated hydrochloric acid, and the temperature kept above the boiling-point of mercury for ten hours. It crystallized out unchanged on cooling.

It also dissolves very readily in dilute alkalies, but no matter how long the alkaline solution is boiled, or how concentrated may be the alkali used, or whether in water or alcoholic solution, acids invariably reprecipitate the unchanged anilide.

The anilide also dissolves in concentrated nitric acid. From this solution, and from its solution in fuming nitric acid, it crystallizes unchanged on dilution, but it is completely decomposed by boiling with fuming nitric acid.

The first decomposition of the substance was effected by means of benzoyl chloride. A small quantity was boiled with benzoyl chloride until it was completely dissolved. The excess of the chloride was then removed as completely as possible by distillation under diminished pressure, and the residue boiled with water. The product, difficultly soluble in water, was crystallized from alcohol, and found to be benzanilide. Its identity was established by means of its melting-point and by comparison with a specimen of benzanilide prepared by the action of aniline on benzoyl chloride. The other product could not be isolated. It was found, however, that if aniline is added to this product the infusible anilide is reformed, indicating that the action of benzoyl chloride, in all probability, consists in replacing at least one of the aniline residues with chlorine. In any case, the formation of benzanilide shows that the infusible anilide contains aniline residues intact, and that no such deep-seated changes are involved in its formation as its indifference to reagents might lead one to suppose.

Phosphorus pentachloride and phosphorus oxychloride likewise react with the anilide, the former in chloroform solution, the latter directly. The products of the reaction are still under investigation.

The experimental evidence thus far obtained does not justify any conclusion as to the structure of the infusible anilide.

Aniline Salt of Orthosulphanilidobenzoic Acid.—This is the fourth aniline derivative of orthosulphobenzoic acid formed by the action of aniline upon orthosulphobenzoyl chloride. Its formation in small quantities is doubtless due to secondary reactions. It crystallizes in long, colorless prisms which, when moist, readily assume a reddish tint in the air; is readily soluble in water and alcohol, difficultly soluble in ether. A sulphur determination gave the following results:

0.1850 gram substance gave 0.1178 gram $BaSO_4$.

0.1624 gram substance gave 0.1042 gram $BaSO_4$.

	Calculated for $C_6H_4<^{CO.ONH_3C_6H_5}_{SO_2NHC_6H_5}$.	Found. I.	II.
S	8.66	8.75	8.81

The salt was also prepared by adding a calculated quantity of aniline to orthosulphanilidobenzoic acid. This method shows that its structure is represented by the formula

$$C_6H_4<^{CO.ONH_3C_6H_5}_{SO_2NHC_6H_5}.$$

Orthotoluenesulphonanilide.—This substance was first prepared by Müller, who gives its melting-point, 136°, but no analysis or further description. As it played an important part in the investigations described above, it was thought desirable to study it somewhat in detail. It was prepared by the action of aniline upon orthotoluenesulphone chloride. A slight excess of aniline was added to the chloride, the mixture warmed on the water-bath, and the excess of aniline removed by distillation in a current of steam. The residue was recrystallized from a mixture of alcohol and water, and the anilide thus easily obtained in a pure state. It melts sharply at 136°, the melting-point given by Müller. It crystallizes in large, colorless prisms, which generally have a tabular development and belong to the orthorhombic system. It is readily soluble in cold alcohol, while it practically mixes in all proportions

with hot alcohol. It is difficultly soluble in ether and water. Heated with water it melts to a heavy oil which, on cooling, solidifies to a crystalline mass. A determination of sulphur and nitrogen gave the following results:

0.1642 gram substance gave 0.1552 gram $BaSO_4$.

0.1428 gram substance gave 0.1362 gram $BaSO_4$.

	Calculated for $C_6H_4<^{CH_3}_{SO_2NHC_6H_5}$	Found. I.	II.	III.	IV.
S	12.97	13.04	13.1	...	...
N	5.68	...	...	5.62	5.56

Like sulphonanilides in general, this substance is very readily soluble in dilute alkalies, differing markedly in this respect from its analogue orthotolanilide, $CH_3.C_6H_4.CONH.C_6H_5$, with which it was compared. Its solution in alkalies is much more stable than that of orthotolanilide. When the alkaline solution of the latter is boiled, the odor of aniline is at once perceptible in the passing steam. The alkaline solution of the sulphonanilide can be boiled for some time before aniline can be detected in the steam, and it requires protracted boiling to decompose a few grams of it completely. This difference between the two classes of anilides is even more marked when they are boiled with dilute acids. Orthotolanilide can be almost completely saponified by boiling with hydrochloric acid (1 to 10). Acid of this dilution has practically no effect upon the sulphonanilide. Five grams of the latter were boiled with 500 cc. of such a mixture for ten hours. On cooling, somewhat more than 4 grams of the unchanged anilide crystallized out; the difference approximately represents the solubility of the sulphonanilide in water. As mentioned in another connection, these facts seem to justify the conclusion that the comparative ease with which one of the aniline residues, in orthosulphobenzanilide, can be removed without disturbing the other, is due to the fact that the former is connected with carbon and the latter with sulphur.

Orthosulphanilidobenzoic Acid.—This substance was obtained by oxidizing orthotoluenesulphonanilide with potassium permanganate in an alkaline solution. The oxidation could not

be made to give anything like a quantitative yield. An attempt was first made to oxidize the sulphonanilide by suspending it, in a finely divided condition, in a considerable quantity of hot water and then adding a solution of potassium permanganate. By this method very little of the anilic acid was obtained, as, in consequence of the insolubility of the anilide and the solubility of the anilic acid, the latter was further broken down, almost as rapidly as it was formed. The best results were obtained by working with small quantities of the anilide in a solution of caustic potash. 5 grams of orthotoluenesulphonanilide were dissolved in a liter of water containing 2 grams of caustic potash, and the solution heated in a bath of boiling water. When the solution had reached the temperature of the bath, permanganate was added, in 5 gram portions, until 20 grams had been added.

This amount of permanganate was not sufficient to oxidize all the anilide used, but the addition of more seemed to affect the product fully as much as the anilide, while by working with the amounts given, the unoxidized anilide could readily be recovered and used in subsequent oxidations. When the color of the permanganate had entirely disappeared, the oxides of manganese were removed by filtering the hot liquid through cloth and paper, and the filtrate was carefully neutralized with hydrochloric acid. The neutralization, at this stage, is rendered necessary by the fact that the anilic acid undergoes considerable decomposition when its alkaline solution is concentrated by evaporation. The neutral solution was then evaporated to a small volume and acidified with concentrated hydrochloric acid. This precipitated both the unchanged anilide and the anilic acid formed. The precipitate was filtered off, thoroughly washed with cold water, and then boiled with an excess of barium carbonate suspended in a liter of water. The solution, containing the barium salt and small quantities of unchanged anilide, was evaporated to dryness, powdered, and repeatedly extracted with small quantities of absolute alcohol to remove the last traces of unoxidized anilide. The barium salt was then crystallized from water and the acid liberated by acidifying with hydrochloric acid. One crystallization from

water of the acid prepared in this way gave a perfectly pure product which melted sharply at 156°.

Orthosulphanilidobenzoic acid is readily soluble in hot water, difficultly soluble in cold water, alcohol, and ether. The analyses of the barium and aniline salts show that its composition is $C_{13}H_{11}O_4N_2S$, and the method of preparation leads to the structure represented by the formula

$$C_6H_4\begin{cases}COOH\\SO_2NHC_6H_5\end{cases},$$

it being formed according to the equation

$$C_6H_4\begin{cases}CH_3\\SO_2NHC_6H_5\end{cases}+3O=C_6H_4\begin{cases}COOH\\SO_2NHC_6H_5\end{cases}+H_2O.$$

Salts of Orthosulphanilidobenzoic Acid.—The salts which orthosulphanilidobenzoic acid forms with the alkalies are all extremely soluble in water and no effort was made to obtain them in pure condition. The barium salt, prepared as mentioned above, crystallizes in small, colorless needles, which usually form in star-like groups and have no well-developed crystal-planes. An analysis gave the following results:

0.2001 gram substance gave 0.0674 gram $BaSO_4$.

0.2251 gram substance gave 0.0763 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{CO.O}_{SO_2NHC_6H_5})_2Ba$.	Found. I.	Found. II.
Ba	19.98	19.8	19.91

Summary.

Briefly stated, the results obtained in this investigation are as follows:

I. The product of the action of phosphorus pentachloride upon salts of orthosulphobenzoic acid is a mixture of two chlorides, one a solid, the other apparently an uncrystallizable oil.

II. The solid chloride is the symmetrical dichloride of orthosulphobenzoic acid represented by the formula $C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases}$.

III. The product of the action of aniline upon the dry, solid chloride is symmetrical orthosulphobenzanil, which has the structure represented by the formula $C_6H_4\begin{cases}CO\\SO_2\end{cases}>NC_6H_5$.

IV. The product of the action of aniline upon the solid chloride in an emulsion of water is symmetrical orthosulphobenzanilide, which has the structure represented by the formula $C_6H_4{<}^{CONHC_6H_5}_{SO_2NHC_6H_5}$.

V. The product of the action of aniline upon the liquid chloride of orthosulphobenzoic acid is the infusible anilide.

III.—SEPARATION OF THE TWO CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

By Ira Remsen and A. P. Saunders.

Although the attempts made by Remsen and Kohler to separate the two chlorides of orthosulphobenzoic acid were not successful it was now decided to undertake further experiments with this object in view. Additional solvents were employed and the crystallizations were carried on at lower temperatures. It so happened that the winter during which this work was done was exceptionally cold and therefore especially favorable for the crystallization. The success of the experiments is in part at least to be ascribed to this fact.

The chlorides are easily soluble in ether and chloroform as stated by Remsen and Kohler, but it has not proved possible to separate them by crystallization from these solvents. They are also very soluble in benzene, toluene, xylene, turpentine, acetone, carbon bisulphide, and glacial acetic acid, but from these solutions only oils are obtained or oily masses containing crystals.

I. *Crystallization of the Chlorides from Petroleum Ether.*

In petroleum ether (boiling-point 80°) the chlorides are very sparingly soluble in the cold, but more readily when the solvent is warmed. The solution of the mixed chlorides in hot petroleum ether, if nearly saturated, becomes milky on cooling, and an oil settles to the bottom. If the vessel be placed in a freezing mixture, the oily mass solidifies, and below a certain temperature the separation of crystals begins. These form a layer at the bottom of the vessel and around the sides, consisting of fine needles of the lower-melting chloride,

associated with the broader, square crystals of the solid. From such a mass, it is impossible to make anything like a satisfactory separation, especially because the needles of the lower-melting chloride melt at once if the hand is brought in contact with the vessel, and in melting, dissolve a considerable portion of the other chloride. It is better in using this method to warm the solution to a point not above 30°, and then to pour off from the chlorides in excess; in this way very little oil separates from the solution before the temperature is reduced to such a point that crystallization begins. But owing to the slight solubility of the chlorides in petroleum ether, only a small quantity is deposited from solution between 10°–15°, where crystallization begins, and 0° or —10°, the temperature to which the solution is cooled; furthermore, when the vessel is plunged into a freezing-mixture and quickly cooled, the crystals that separate are very minute and not well formed. Hence the best method of obtaining pure crystals is to cool down to about 0°, and then cause evaporation to take place; the most favorable conditions are those in which the solution can be placed out of doors and allowed to stand over night or for a couple of days; if the temperature remain at 0° or below, fine crystals are obtained.

The higher-melting chloride forms square, hollow crystals, similar in shape to those produced by recrystallization from ether, only the latter are better formed and not hollow. The melting-point is 76°–77° uncorr. The lower-melting chloride forms radiating clusters of delicate, glistening white needles, sometimes as much as three to four centimeters in length. The melting-point of these crystals is 21.5°–22.5° uncorr.

The conditions of the open air can be imitated by keeping the beakers used for crystallization in running water or in a freezing mixture and drawing air over the surface of the liquid; in this way good crystals of both chlorides can be obtained.

Although the lower-melting chloride generally begins to form crystals at about 10° when separating from solution, it has been found advisable in all crystallizations to add a nucleus of a few crystals, or a small fragment of the mixed chlorides in the solid form, as soon as the solvent has cooled

down to 10°–15°, a point at which there is no danger that the nucleus itself will be melted. Several recrystallizations were found necessary in order to obtain either one of the chlorides quite pure.

It will be seen that the above method is tedious to carry out and gives only a small yield of pure products in the end, so that where large quantities are desired there is, as yet, no means of obtaining the lower-melting chloride in pure condition, though the higher-melting chloride can be readily obtained pure by the following method, devised by Mr. J. E. Bucher, in this laboratory:

To a convenient quantity of chlorides dissolved in chloroform, concentrated aqueous ammonia is added, and the solutions shaken together for about a minute; the chloroform solution is then drawn off, and, on evaporation, yields pure solid chloride;[1] the liquid chloride is converted by ammonia into a substance soluble in water, whereas, the solid chloride is much less readily attacked.

At the time when the experiments recorded in the following pages were carried out this method was not known, and there was no test for the purity of the samples of the liquid chloride used excepting (1) the melting-point, which does not suffer much change from the presence of even a considerable percentage of solid chloride, and (2) the number of recrystallizations to which the chloride had been subjected; it should, therefore, be stated that while the solid chloride used in the experiments was almost or quite pure, the liquid chloride contained, as a rule, some of the solid; the reactions generally indicate this, but the results are rarely ambiguous.

It seemed likely that there might be some difference in the solubility of the two chlorides in petroleum ether, and that a separation might be effected by treatment with successive portions of the solvent. A quantity of the mixed chlorides was, therefore, treated with six successive washings of warm petroleum ether, and these were then left to stand in a cool room and evaporate spontaneously; from each of the six solutions both chlorides were obtained, and it did not appear that any separation could be brought about by this means.

[1] The names solid chloride and liquid chloride will be used for the present, although both substances are solid at low temperatures.

In these crystallizations a separation of light flakes of white needles insoluble in petroleum ether was frequently observed, and the same substance sometimes appears in the chlorides when they are allowed to stand for some time. These needles were found to be soluble in hot water, separating again as the solution cools; they then melt at 137°, and are undoubtedly orthochlorbenzoic acid, since Remsen and Kohler found that orthochlorbenzoyl chloride is produced either by the action of phosphorus pentachloride on the chlorides of orthosulphobenzoic acid at temperatures above 100°, or by merely heating the chlorides themselves to a somewhat higher point. A certain amount of decomposition goes on during the process of crystallization from petroleum ether by which orthosulphobenzoic acid is obtained; the darkening of color which takes place in solutions which are left exposed is probably due to the charring of particles of dust which find their way in from the air.

Analyses of the Chlorides.—Portions of both chlorides were decomposed in beakers by warming with concentrated nitric acid to which a solution of silver nitrate had been added.

I. 0.2981 gram solid chloride gave 0.3578 gram AgCl.

	Calculated for $C_7H_4SO_3Cl_2$.	Found.
Cl	29.65	29.68

This agrees with the results of Remsen and Kohler, who found in two analyses 29.46 and 29.4 per cent. of chlorine.

I. 0.1112 gram liquid chloride gave 0.1333 gram AgCl.

II. 0.2546 gram liquid chloride gave 0.3109 gram AgCl.

	Calculated for $C_7H_4SO_3Cl_2$.	Found. I.	Found. II.
Cl	29.65	29.64	30.19

II. *Action of Water on the Chlorides.*

Action in the Cold.—In the cold, water acts with extreme slowness on both of the chlorides.

Two grams of each chloride were placed in 100 cc. of water in a small flask; decomposition began at once, as was shown by testing the water with silver nitrate, but was not complete until about three months had elapsed. The solutions were left to stand over summer, and were then treated with silver carbonate in the hope that, as they had not been heated, it might be possible to obtain two kinds of silver salts; but on

allowing the solutions to evaporate spontaneously, similar crystals were obtained from each, and there was no indication of the formation of two substances.

Action on Heating.—In hot water the chlorides are not rapidly decomposed, but, on boiling, reaction soon sets in, and decomposition is complete after five to ten minutes when small quantities are used; neither in this reaction, nor where the decomposition went on in the cold, was any characteristic difference noted in the rate of reaction for the two substances. From the acids obtained by boiling the chlorides separately with water, barium salts were obtained identical in appearance, behavior, and in composition, as the analyses show.

0.1021 gram neutral barium salt from the acid obtained by decomposition of the solid chloride gave 0.0631 gram $BaSO_4$.

	Calculated for $C_7H_4SO_4Ba+2H_2O$.	Found.
Ba	36.73	36.35

0.1278 gram neutral barium salt from the acid obtained by decomposition of the liquid chloride gave 0.0807 gram $BaSO_4$.

	Calculated for $C_7H_4SO_4Ba+2H_2O$.	Found.
Ba	36.73	37.14

III. *Action of Ammonia on the Chlorides.*

Aqueous Ammonia.—Both chlorides, when heated with dilute ammonia, gave solutions which had an intensely sweet taste, and from which, on acidifying, crystals identical in appearance and having the characteristic taste of benzoic sulphinide were obtained. Mr. A. D. Chambers, working in this laboratory, has recently studied the action of concentrated ammonia on the chlorides in the cold, and finds that two substances are formed; the one from the liquid chloride is probably the ammonium salt of an acid having the formula,

$$C_6H_4\begin{cases} CN \\ SO_3OH \end{cases}.$$

Dry Ammonia Gas. — The following experiments are of interest as showing that the above substance is only obtained from the liquid chloride.

1. Dry ammonia gas was passed into an ether solution of 0.5 gram of the solid chloride. A white precipitate was

formed in the ether, probably ammonium chloride. When the ether was allowed to evaporate, a crystalline residue, which had an intensely sweet taste was obtained. When treated with water, this all went into solution, and on the addition of hydrochloric acid, saccharine separated.

2. Dry ammonia gas was passed into an ether solution of 0.7 gram liquid chloride; a white precipitate separated as above. On evaporation, a crystalline mass was obtained which tasted slightly of saccharine; this went into solution readily in water; on addition of hydrochloric acid, no crystals were obtained, but on warming over the water-bath, a few crystals of saccharine separated.

These solutions were then left to stand and were not again studied until after the experiments of Mr. Chambers, mentioned above. When both solutions had completely evaporated, that from the solid chloride gave a mixture containing ammonium chloride and saccharine as a white crystalline mass, whereas that from the liquid chloride gave ammonium chloride and radiating compact masses of brownish needles, very soluble in water, having a bitter taste, and melting at about 115°. They are very soluble also in alcohol, and from that solvent are obtained as white botryoidal masses of minute needles melting at 116°–120°. The yield, after recrystallization, was 0.45 gram. These crystals are evidently identical with those discovered by Mr. Chambers, and are apparently not produced at all from the solid chloride; on the other hand, the formation of a slight quantity of saccharine from the liquid chloride may have been due either to the presence in it of some of the solid chloride, or to a transformation of the compound $C_6H_4\begin{cases}CN\\SO_2.OH\end{cases}$ into saccharine.

IV.—*Action of Phenol on the Chlorides.*

Action on The Mixed Chlorides.—When the mixed chlorides are added to phenol they pass into solution, but in the cold no reaction takes place. On warming, however, the evolution of hydrochloric acid begins at once, and the liquid assumes a clear lake-red color, which becomes more and more intense as the reaction proceeds. If the reaction is allowed to go on quietly to the end, with occasional momentary heating over

the flame, a viscous, opaque red mass is obtained, which becomes thick and gummy when cold. If it is poured, while hot, into a solution of sodium hydroxide, it at once takes on the characteristic color of phenolphthalein—an intese purple; at the same time a portion separates as an insoluble crystalline cake and can, by filtration and washing with water, be obtained quite free from the colored substance. This crystalline substance is readily soluble in hot alcohol, sparingly in cold, insoluble in water, and crystallizes from alcohol in shining leaflets or slender flat needles which melt at 117.5°–118.5° uncorrected.

When boiled with a concentrated solution of potassium hydroxide it melts and is ultimately decomposed, for, on acidifying, the odor of phenol is plainly perceived, and when bromine water is added a considerable deposit of tribromphenol is formed. The substance gave, on analysis, the following results:

I. 0.1753 gram gave 0.4156 gram CO_2 and 0.0754 gram H_2O.

II. 0.0917 gram gave 0.2150 gram CO_2 and 0.0381 gram H_2O.

III. 0.1579 gram gave 0.3731 gram CO_2 and 0.0645 gram H_2O.

IV. 0.1696 gram gave 0.3974 gram CO_2 and 0.0670 gram H_2O.

V. 0.1934 gram gave 0.1309 gram $BaSO_4$.

VI. 0.1820 gram gave 0.1194 gram $BaSO_4$.

	Calculated for $C_{19}H_{14}SO_5$.	Found. I.	II.	III.	IV.	V.	VI.
C	64.41	64.65	63.95	64.44	63.91	....	....
H	3.95	4.78	4.61	4.54	4.39	....	....
S	9.04	....	....	....	....	9.34	9.02

From the analytical results, the method of formation, and the chemical behavior of this compound, it appears that it is the diphenyl ether of orthosulphobenzoic acid, of the formula

$$C_6H_4\begin{cases}CO.OC_6H_5\\SO_2.OC_6H_5\end{cases}.$$

The combustions of this substance and of all others analyzed were made by the lead chromate method, as described by De

Roode.[1] The sulphur determinations were made by the Liebig method, excepting in two cases where it was found necessary to use that of Carius.

Action on the Solid Chloride.—When the pure solid chloride is heated with phenol, hydrochloric acid is given off. If the reaction is checked after a few moments, the product is almost entirely the phenol ether above described, though there is also formed at the same time some of the colored substance.

1 gram of pure chloride gave in this way 0.6 gram of phenol ether. If, however, the boiling is continued for some time longer, the reaction seems to enter on a second stage, with the formation of a larger quantity of the colored product. 2.3 grams heated for ten minutes gave only 0.5 gram of phenol ether and more than 1 gram of the red compound.

Action on the Impure Liquid Chloride.—A small quantity of the liquid chloride, containing also some of the solid, was heated for a short time with phenol. The usual color was obtained, though it was not very intense, and on pouring the liquid into dilute alkali, a heavy yellow oil settled to the bottom; this became crystalline after some time, and on recrystallization from alcohol yielded two products; one in leaflets identical in appearance with the phenol ether; the other in clear thin columns melting at 98°–100° uncorrected.

V.—*Action of Benzene and Aluminum Chloride on the Chlorides.*

The benzene used in these experiments was dried over sodium. The aluminium chloride was, for the most part, the commercial resublimed product; it was always used in these reactions in about the proportions given below (page 362).

When aluminium chloride is added to a solution of the mixed chlorides in benzene, reaction begins at once. At first, bubbles of hydrochloric acid are given off slowly, but after a few moments the solution becomes warmer and reaction sets in vigorously; by plunging the vessel in cold water the evolution of hydrochloric acid is much retarded, but on warming again, even in the hand, it at once resumes its former activity. It has proved possible by controlling this reaction to get different products.

[1] This Journal, 12, 226.

1.—*Action on the Mixed Chlorides in the Cold.*—On leaving the vessel in which the reaction goes on, in cold water, hydrochloric acid is given off gently for twenty minutes or half an hour. There then remains an almost or quite opaque red solution, with sometimes a heavy opaque layer separated at the bottom. If this liquid is now poured into a small quantity of dilute hydrochloric acid cooled, or containing pieces of ice, and stirred vigorously for a few moments, the color disappears, the water becomes cloudy, and a layer of almost colorless benzene floats on the top; this is poured off and quickly evaporated. When the benzene is all driven off there remains a clear viscous oil, which if left to stand, crystallizes after some time forming a solid dry cake; solidification can be quickly induced by rubbing with a rod. Care must be taken not to heat longer than is necessary in driving off the benzene, as decomposition is apt to take place. The crystalline mass obtained is insoluble in water, but dissolves readily in ether if powdered and shaken with that solvent; from this solution, by spontaneous evaporation, fine crystals are obtained with very well-developed faces. Their melting-point is 96°–97° uncorrected. This substance is soluble in alcohol, ether, and benzene, sparingly in petroleum ether. It appears to be a compound in which one of the chlorine atoms of orthosulphobenzoyl chloride has been replaced by a phenyl group.

I. 0.2322 gram gave 0.1183 gram AgCl.
II. 0.1367 gram gave 0.0695 gram AgCl.
III. 0.1775 gram gave 0.1470 gram $BaSO_4$.
IV. 0.1363 gram gave 0.1137 gram $BaSO_4$.

	Calculated for $C_{13}H_9SO_3Cl$.	Found. I.	II.	III.	IV.
Cl	12.66	12.60	12.58	....	....
S	11.41	....	....	11.39	11.46

There are several possible formulas for a substance of this composition, but its reactions and decompositions show that it is in all probability derived from the symmetrical chloride of orthosulphobenzoic acid by the substitution of phenyl for the chlorine atom connected with carbon, as represented by the formula, $C_6H_4\begin{cases}CO.C_6H_5\\SO_2.Cl\end{cases}$. In accordance with this view

the name orthobenzoylbenzenesulphone chloride is given to the substance.

According to the theory of the structure of the two chlorides of orthosulphobenzoic acid it is to be expected that two different substances might be produced in the reaction with benzene and aluminium chloride in the cold. All efforts to obtain a second product from this reaction have so far been unsuccessful. When the product is recrystallized from ether there is always a certain amount of a heavy oily substance produced, but this appears to be the acid, identical with that obtained when pure orthobenzoylbenzenesulphone chloride is boiled with water.

The reaction with benzene and aluminium chloride is always accompanied by the formation of colored products. If the vessel in which the reaction has been performed is allowed to stand for a day, the residues turn a fine violet or green color.

Orthobenzoylbenzenesulphone Chloride, when left exposed to the air, absorbs water and decomposes, yielding a thick liquid not unlike the aqueous solution of orthosulphobenzoic acid. If allowed to stand in cold water the chloride is not immediately attacked, but if boiled for about ten minutes decomposition is complete. In this way an acid solution is obtained which at first gives no crystals even when evaporated until it is syrupy; but, if then allowed to stand for some time, long transparent crystals are formed. According to the above view this acid has the structure represented by the formula $C_6H_4\begin{smallmatrix}/\,CO.C_6H_5\\ \backslash\,SO_2.OH\end{smallmatrix}$.

Potassium Orthobenzoylbenzenesulphonate.—The acid solution above mentioned, when neutralized with potassium hydroxide, gives a very soluble potassium salt which crystallizes well from concentrated aqueous solution, but better from alcohol, in which it is somewhat less soluble. The crystals thus obtained are very well formed, with perfect faces. When crystallized either from water or from 95-per cent. alcohol the substance, when quickly heated, melts at 122°–124°, but if it is slowly heated the melting-point rises to about 175°.

I. 0.4569 gram of the crystals obtained from water, when heated for eight hours at about 115°, lost 0.0264 gram. The calculated loss for one molecule of water from the compound $C_{13}H_9SO_4K + H_2O$ is 0.0275 gram.

II. 0.7479 gram of the crystals obtained from alcohol, heated in the same way lost 0.0427 gram. The calculated loss is 0.0423 gram.

The melting-point of the dried salt is 181.5°–182.5° uncorr.

On analysis the following results were obtained for the hydrated salt:

I. 0.1742 gram gave 0.1327 gram $BaSO_4$.
II. 0.1630 gram gave 0.1233 gram $BaSO_4$.
III. 0.1597 gram gave 0.1172 gram $BaSO_4$.
IV. 0.2145 gram gave 0.0582 gram K_2SO_4.
V. 0.1702 gram gave 0.0461 gram K_2SO_4.

	Calculated for $C_{13}H_8SO_4K+H_2O$.	Found.				
		I.	II.	III.	IV.	V.
S	10.06	10.47	10.40	10.09	...	...
K	12.26	...	...	...	12.16	12.15

From the anhydrous salt the following result was obtained: 0.1973 gram gave 0.1556 gram $BaSO_4$.

	Calculated for $C_{13}H_9SO_4K$.	Found.
S	10.67	10.85

This potassium salt can be more easily obtained by allowing the chloride itself to react directly with caustic potash, with application of a very little heat; in this way a solid mass of the salt is at once obtained.

If the salt is further heated with dry potassium hydroxide, it decomposes almost quantitatively, yielding benzoic acid and benzenesulphonic acid. When the products of decomposition are dissolved in water, and this solution acidified the benzoic acid is precipitated in small white crystals which, when separated on the filter, washed, and dried, melt at 120°. They dissolve in hot water and give the characteristic odor of benzoic acid; they sublime, forming the well-known delicate laminæ, and giving at the same time the usual odor. The filtrate, when evaporated to dryness, yields a mixture of potassium chloride and a more soluble salt. On treatment with phosphorus pentachloride an oil is obtained having the peculiar odor of benzenesulphone chloride, and this oil, when treated with ammonia, gives an amide sparingly soluble in water in the cold, more readily on warming, and melting

at 145°–147°. The melting-point of benzenesulphone amide when pure, is 149°.

This decomposition of potassium orthobenzoylbenzenesulphonate is therefore to be represented by the equation

$$C_6H_4\begin{cases}CO.C_6H_5\\SO_2.OK\end{cases}+KOH=C_6H_5.SO_2.OK+C_6H_5.CO.OK.$$

Ethyl Ether of Orthobenzoylbenzenesulphonic Acid.—The chloride of this acid, as mentioned above, is soluble in alcohol and crystallizes from that solvent; but when a recrystallization was attempted a new product was obtained, having the melting-point 125.5°–126.5° uncorr. On attempting to prepare a quantity of this substance no satisfactory results were obtained. Several grams of the chloride, when heated with absolute alcohol on the water-bath for a day, yielded on evaporation only free acid; furthermore, the ethyl ether itself on recrystallization from alcohol gradually decomposes, giving the free acid again. This is in accordance with the recent work of Krafft and Roos,[1] who found that benzenesulphone chloride was transformed into the acid by treatment with alcohol. The ethyl ether was obtained on crystallizing the chloride from a mixture of ether and alcohol by allowing the solution to stand for a few days. This tendency to pass over into the acid may account for the very high figures obtained for hydrogen in combustion.

The analysis of the compound yielded the following results:

I. 0.1233 gram gave 0.2827 gram CO_2 and 0.0640 gram H_2O.

II. 0.1192 gram gave 0.2736 gram CO_2 and 0.0647 gram H_2O.

III. 0.1781 gram gave 0.1409 gram $BaSO_4$.

IV. 0.1739 gram gave 0.1392 gram $BaSO_4$.

	Calculated for $C_{12}H_{10}SO_4$.	Found. I.	II.	III.	IV.
C	62.07	62.53	62.60	....	....
H	4.83	5.78	6.04	....	....
S	11.03	....	....	10.88	11.01

Lactim of Orthobenzoylbenzenesulphonic Acid.—It was at first supposed that the action of ammonia on the chloride of this

[1] Ber. d. chem. Ges., **26**, 2827.

acid would furnish an amide of the formula $C_6H_4\begin{matrix}CO.C_6H_5\\SO_2.NH_2\end{matrix}$ and in order to obtain this compound some of the chloride in ethereal solution was subjected to the action of dry ammonia gas. A separation of ammonium chloride occurred at once, and after a few minutes the reaction was complete. The ethereal solution was filtered off and evaporated to dryness. The product thus obtained is a crystalline substance insoluble in water, sparingly soluble in cold alcohol, more readily in hot, and crystallizing from that solvent in flat leaf-like plates which are quite white, and melt at 163° uncorr. The results of the analyses are given below:

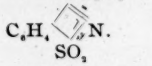
I. 0.1454 gram gave 0.3437 gram CO_2 and 0.0555 gram H_2O.
II. 0.0928 gram gave 0.0914 gram $BaSO_4$.
III. 0.1362 gram gave 0.1362 gram $BaSO_4$.
IV. 0.2065 gram gave 10.01 cc. nitrogen.[1]

	Calculated for $C_{13}H_9SO_2N$.	Found. I.	II.	III.	IV.
C	64.20	64.47	...	...	...
H	3.70	4.24	...	...	...
S	13.17	...	13.54	13.75	...
N	5.76	...	...	...	6.01

That the substance is not the amide is plainly shown by the above results; the values calculated for the amide of the formula given are:

$$C = 59.77;\ H = 4.21;\ S = 12.26;\ N = 5.36.$$

The formation of a lactin in this way accords with the general behavior of such aromatic amides of the ortho series; the formula of the compound thus produced by loss of water from the amide is in all probability,



Anilide of Orthobenzoylbenzenesulphonic Acid.—When the chloride of the acid is heated for a few minutes with aniline and then poured into moderately concentrated hydrochloric acid, a gummy mass is obtained which, when the aniline is

[1] The estimation of nitrogen was kindly made for us by Mr. G. W. Gray, of this laboratory, using the absolute method.

all dissolved out, becomes solid and crystalline. By filtering and washing, the crystalline product is obtained fairly pure. It is moderately soluble in hot alcohol, sparingly in cold, and crystallizes in flat narrow blades or needles which melt at 143°–145° uncorr. At the same time short square crystals are formed which have the same melting-point, and are probably only another form of the same substance. An analysis of the needles gave the following results:

0.0924 gram gave 0.0669 gram $BaSO_4$.

	Calculated for $C_{19}H_{15}SO_3N$.	Found.
S	9.56	9.95

Structure of the Compounds described above.—The structure of these compounds is clearly shown by the following considerations:

1. The very easy solubility of the acid obtained by the decomposition of the chloride with water. Such sulphonic acids are in general readily soluble, whereas the analogous carboxyl acids are sparingly soluble.

2. The decomposition of the potassium salt on fusion with potassium hydroxide by which benzoic acid and benzenesulphonic acid result. It is possible to imagine the formation of these products from either of the substances

$$C_6H_4\begin{cases}CO.C_6H_5\\SO_2.OK\end{cases} \quad \text{and} \quad C_6H_4\begin{cases}CO.OK\\SO_2.C_6H_5\end{cases},$$

but diphenylsulphone itself, when fused with potassium hydroxide, breaks down in a complicated way, giving several different products, including phenol, diphenyl, and sulphur dioxide. Furthermore, the reaction is not very readily brought about, whereas in the above case the decomposition is perfectly smooth and clean. It will also be shown later that a substance having the probable formula $C_6H_4\begin{cases}CO.C_6H_5\\SO_2.C_6H_5\end{cases}$ breaks down under similar circumstances, giving benzoic acid and diphenylsulphone.

3. The fact that the ethyl ether suffers gradual decomposition in the presence of alcohol, giving the free acid again, accords much better with the supposition that the acid is a sulphonic acid than that it is a carboxyl acid.

4. The formation of a lactim is also an argument in favor of the presence of the ketone group.

2. *Action of Benzene and Aluminium Chloride on Orthobenzoylbenzenesulphone Chloride.*—2 grams of the chloride were dissolved in benzene and about 3 grams of aluminium chloride added. The reaction was scarcely perceptible when the heat of the hand only was applied, but after warming a moment in the flame the reaction went on briskly. At the end the solution was poured into water as usual. In this way a certain amount of tarry material was obtained, but the benzene solution, on evaporation, gave a mass of crystals which, when recrystallized from alcohol, melted at 183°–185°, and had the appearance of a compound of the same melting-point which will be described below, and which is obtained as the end-product of the action of benzene and aluminium chloride on the solid chloride of orthosulphobenzoic acid. The yield corresponded to about 55 per cent. of that calculated.

This shows orthobenzoylbenzenesulphone chloride to be an intermediate product of the action of benzene and aluminium chloride on one of the chlorides of orthosulphobenzoic acid, probably the solid, as will appear.

3. *Action on the Pure Solid Chloride of Orthosulphobenzoic Acid.*—The reaction in the case of all these chlorides is singularly variable; slight differences of temperature appear to cause serious variations in the results obtained, and probably the purity of the materials is also an important factor.

The pure solid chloride does not enter into reaction as readily as the mixed chlorides. It does, however, react slowly when warmed in the hand, and this reaction when carried out as previously directed gives rise to the formation of orthobenzoylbenzenesulphone chloride, though the yield is not large, as some of the material goes over into a gummy mass from which nothing definite was obtained, and in some cases nothing but gummy material was produced.

2 grams of pure solid chloride gave about 1 gram of orthobenzoylbenzenesulphone chloride.

4. *Action on the Mixed Chlorides when Heated.*—This reaction, which was the first one used, was studied for a long time and under a variety of conditions in the hope that two distinct

products might be obtained from it, but, although the crystalline product mentioned as being obtained by the action of orthobenzoylbenzenesulphone chloride was invariably produced, it has never proved possible to obtain a corresponding product from the liquid chloride, though, as will be shown later, there are indications that an isomeric product was obtained when the latter chloride in very pure condition, was used.

The reaction with the mixed chlorides goes on best in this way: 10–20 grams of chloride are dissolved in four or five times that weight of benzene in a large test-tube or a beaker, and to the solution, aluminium chloride is added in two or three quantities until the weight is about equal to that of the chloride used. Heat is then applied to the vessel from time to time, by which the reaction is accelerated. After about twenty minutes it is complete. If the solution is now heated again and removed, the evolution of gas ceases at once; nor does further addition of aluminium chloride cause a renewal of the reaction. The end may be recognized in this way:

The product so obtained is an opaque, or nearly opaque, red liquid, with a heavy layer, almost black, at the bottom. The whole mass is poured into hot water. If any aluminium chloride is present in excess it is violently attacked, and that which has entered into reaction is set free, with evolution of a good deal of heat. By this means the benzene present is almost entirely driven off; the last portions are expelled by further heating. The product thus obtained is a brownish, granular mass, the color of which varies in different instances. It is sometimes pale and semi-crystalline; at others, darker and gummy. By filtering and washing, all the aluminium is got rid of, and the substance may be dried and recrystallized from hot alcohol, in which it is somewhat soluble, though almost insoluble in cold. The product thus obtained is, as a rule, more or less colored, either brown or dull violet, and this color is very difficult to get rid of either by boiling with animal charcoal or by recrystallization. Even the purest samples were still slightly colored. When crystallized slowly from alcohol it forms leaflets of irregular surface, generally terminated by an obtuse angle. These melt at 183.5°–184° uncorr.

Better crystals are obtained from benzene, in which it is more readily soluble. It is sparingly soluble in ether, and quite insoluble in water; it dissolves in concentrated nitric acid and in concentrated sulphuric acid, and is obtained unchanged from both. Analyses gave the following results:

I. 0.1850 gram gave 0.4792 gram CO_2 and 0.0826 gram H_2O.

II. 0.1692 gram gave 0.4433 gram CO_2 and 0.0738 gram H_2O.

III. 0.1341 gram gave 0.0915 gram $BaSO_4$ (Carius).

IV. 0.1303 gram gave 0.0984 gram $BaSO_4$.

V. 0.1882 gram gave 0.1377 gram $BaSO_4$.

	Calculated for $C_{19}H_{14}SO_3$.	Found. I.	II.	III.	IV.	V.
C	70.81	70.65	71.45	....	....	....
H	4.35	4.96	4.84	....	....	....
S	9.94	....	....	9.39	10.37	10.06

From the method of preparation it seemed likely that this substance was a diphenyl derivative having the structure represented by the formula $C_6H_4\begin{matrix}CO.C_6H_5\\ SO_2.C_6H_5\end{matrix}$. This view is confirmed by the properties and reactions of the compound.

It is stable in the presence of ordinary reagents. As mentioned above, it dissolves undecomposed in strong nitric and sulphuric acids; a mixture of fuming nitric acid and sulphuric acid, heated to boiling, attacks it with the formation of a non-crystalline yellow product, soluble in alcohol. Alcoholic potash has no action even when the substances are boiled together for a day. The compound may be heated alone to 250° without change, but at a somewhat higher temperature it sublimes with slight decomposition; the sublimate consists of the original substance.

When fused with potassium hydroxide it is decomposed, and this reaction furnishes the strongest evidence in favor of the structural formula given above. If the substance is heated slowly with caustic potash in excess, the reaction takes place rapidly at 200°–210°, with formation of a yellowish-brown mass. This, when warmed with water, partially dissolves. The residue, separated by filtration and recrystalliza-

tion from alcohol, gives the characteristic rhombic crystals of diphenylsulphone, melting at 123°–124° and having the solubility and general character of that compound. The filtrate treated with hydrochloric acid gives a precipitate of benzoic acid. The results are nearly quantitative.

The benzoic acid obtained in this way melts at 119°–120°, is soluble in hot water, giving the usual odor, and separates out in small crystals as the solution cools; it sublimes in thin leaflets, and shows in every way the properties of benzoic acid. The identity of the diphenylsulphone was at first questioned on account of a discrepancy between its melting-point and that given for the substance in Beilstein's Handbuch, where the melting-point 128°–129° is quoted from Otto,[1] who prepared it by the action of benzenesulphone chloride on mercury diphenyl. But in an earlier article,[2] Otto gives the melting-point of a quantity prepared by the action of benzenesulphone chloride on benzene and aluminium chloride as 124°. Other observers give various other values; as 125°–126°,[3] 126°,[4] 128°.[5]

To determine, if possible, whether the variations were due to differences of purity, about 20 grams of diphenylsulphone were carefully investigated. The substance was prepared by Dr. R. M. Parks, in this laboratory, by the action of benzene and aluminium chloride on benzenesulphone chloride. It was already fairly pure, and melted after one recrystallization at 122.5°–124°. It was then subjected to six recrystallizations from alcohol and from alcohol and water, and the melting-point taken from time to time. This varied very little, and the substance finally obtained, which had the appearance of a perfectly pure product, melted at 122.5°–123.5° uncorr.

The decomposition above referred to takes place, no doubt, according to the equation

$$C_6H_4\begin{matrix}CO.C_6H_5\\SO_2.C_6H_5\end{matrix} + KOH = C_6H_5SO_2.C_6H_5 + C_6H_5.CO.OK.$$

[1] Ber. d. chem. Ges., **18**, 248.
[2] *Ibid*, **11**, 2066.
[3] Knapp: Ztschr. Chem., 1869, 41.
[4] Stenhouse: Ann. Chem. (Liebig), **140**, 290.
[5] Freund: *Ibid*, **120**, 81.

In accordance with this view the substance is named orthobenzoyldiphenylsulphone. If it has the above structural formula, it is, in one sense, a ketone, and it was expected that it would yield the usual derivatives with phenylhydrazine and with hydroxylamine. Several attempts were made to bring about the formation of such products, but in vain.

5. *Action on the Pure Solid Chloride when Heated.*—One gram of pure solid chloride, when submitted to reaction and several times warmed, yielded a certain amount of gummy material and 0.7 gram of crystalline product, which, when dissolved in alcohol, deposited 0.4 gram pure orthobenzoyldiphenylsulphone; hence the yield corresponds in this reaction to about 50 per cent. of the calculated quantity, and could no doubt be increased by carefully regulating the conditions. The facts described show clearly that this substance is derived from the solid chloride. It then becomes a matter of great interest to determine, if possible, what becomes of the liquid chloride in the reaction on the mixed chlorides. As mentioned above, no definite product has as yet been obtained from that reaction, corresponding to the liquid chloride. The water in which the benzene is poured after the reaction, has several times been evaporated, but yields little or nothing but inorganic substances.

There is always a quantity of gummy or tarry material formed which is more soluble in alcohol than the benzoyldiphenylsulphone, and this can be washed out with warm alcohol. On evaporation only the original gum is obtained. On sublimation of this, a substance is given off at a high temperature and crystallizes on the sides of the vessel in yellow needles, while, at the same time, an oil is also obtained, which was not further studied. The yellow needles, which melt at 205°–207°, with previous softening, are somewhat soluble in hot alcohol, sparingly in cold. The solution is yellow by transmitted light, and brilliant blue by reflected light. On recrystallization the yellow color almost entirely disappears, but the blue fluorescence remains, and is apparently due to the compound itself and not to an impurity.

6. *Action on the Liquid Chloride when Heated.*—It was only in the early stages of this investigation that any considerable

quantity of the liquid chloride in pure condition was available. At that time the purest samples gave very little if any orthobenzoyldiphenylsulphone, but yielded mostly gummy or tarry masses from which very little could be obtained. A few crystals were produced at one time which had a different habit, and melted at 161°–162° uncorr. Many efforts have since been made to prepare a further quantity of this product, but always without success. That on hand was finally purified as well as possible, with so small a quantity, and submitted to analysis, with the following results:

I. 0.1223 gram gave 0.3122 gram CO_2 and 0.0537 gram H_2O.

II. 0.0827 gram gave 0.0665 gram $BaSO_4$.

	Calculated for $C_{19}H_{14}SO_3$.	Found. I.	II.
C	70.81	69.63	....
H	4.35	4.88	....
S	9.94	....	9.39

These results, though not satisfactory, indicate that the substance is probably an isomer of orthobenzoyldiphenylsulphone, perhaps a substance of the formula

$$C_6H_4\begin{cases}C(C_6H_5)_2\\SO_2\end{cases}O.$$

When dropped into fusing caustic potash the compound reacts, giving an intense carmine color. This suggests the possible formation of such a triphenyl-methane derivative as

$$C_6H_4\begin{cases}C(C_6H_5)_2.OH\\SO_2.OH\end{cases} \quad \text{or} \quad C_6H_4\begin{cases}C(C_6H_5)_2OH.\\OH\end{cases}$$

Summary.

The main results reached in this investigation may be summarized as follows:

1. It has been found possible by the use of petroleum ether to separate two chlorides of orthosulphobenzoic acid in crystalline form; one melts at 21.5°–22.5° uncorr., the other at 76°–77° uncorr. The latter was already known in crystalline form, and the existence of a second chloride had been indicated by the reactions of the mixed chlorides. Both of these chlorides, when heated with water, give orthosulphobenzoic acid; and the same results have always thus far been obtained

when they are allowed to decompose in the presence of water in the cold.

2. When treated with ammonia, the pure solid chloride gave saccharine and ammonium chloride, and no other product could be detected; the liquid chloride, on the other hand, gave saccharine in part, but also a large yield of a second product which is probably the ammonium salt of orthocyanbenzenesulphonic acid.

3. When treated with phenol, both chlorides apparently have a tendency to go over finally to a colored substance like phenolphthalein, but yield crystalline products if the reaction is checked after a few moments. In this way, from the mixed chlorides, and from the pure solid chloride, the normal phenyl ether of orthosulphobenzoic acid is obtained, having the formula $C_6H_4\begin{cases}CO.OC_6H_5\\SO_2.OC_6H_5\end{cases}$.

4. By the action of the mixed chlorides on benzene and aluminium chloride a product is first formed which is, apparently, orthobenzoylbenzenesulphone chloride, $C_6H_4\begin{cases}CO.C_6H_5\\SO_2.Cl\end{cases}$.

This decomposes with water, giving a very soluble acid, which yields characteristic salts.

The same compound is obtained when the pure solid chloride is used, whence it appears probable that in its formation from the mixed chlorides it comes from the solid and not from the liquid.

5. By continued action of benzene and aluminium chloride on the chlorides or on this intermediate product, orthobenzoyldiphenylsulphone, $C_6H_4\begin{cases}CO.C_6H_5\\SO_2.C_6H_5\end{cases}$, is obtained.

The same product is also formed when the pure solid chloride is used in the reaction and the substances heated together.

Hence from the solid chloride it is possible to pass at once to orthobenzoyldiphenylsulphone; or the intermediate product, orthobenzoylbenzenesulphone chloride, may be formed, and this, by further action, may be transformed into orthobenzoyldiphenylsulphone.

These reactions all speak in favor of the symmetrical for-

mula $C_6H_4\begin{cases}CO.Cl\\SO_2.Cl\end{cases}$ for the solid chloride of orthosulphobenzoic acid.

In favor of the formula $C_6H_4\begin{cases}CCl_2\\SO_2\end{cases}O$ for the liquid chloride there is, as yet, little direct evidence. Nevertheless, its action with ammonia and the formation, though in small quantity, of the product described in the text, by reaction with benzene and aluminium chloride, are worthy of attention.

Contributions from the Chemical Laboratory of Purdue University.

XIV. THE SUGAR OF THE *AGAVE AMERICANA*.

By W. E. Stone and D. Lotz.

Under the title of "Researches on the Sugar of the *Agave Americana*," Messrs. Gustave Michaud and José Fidel Tristan have published in this Journal, **14**, 548, a paper which the authors summarize as follows: "The *Agave Americana* contains a sugar of the formula $C_{12}H_{22}O_{11}$. This sugar differs from all others of the same group except synanthrose, by its inactivity. It differs from synanthrose by its power of crystallizing, by its action on Fehling's solution and by the rotatory power of the products of its inversion. We propose for the sugar the name of *Agavose*."

An inspection of the data presented by the authors, suggested to one of us that, with one exception (the optical inactivity), the properties of agavose were strikingly like those of sucrose under the same conditions. For instance, the authors state that the juice obtained by pressing the leaves of the agave, after treatment with alcohol, basic acetate of lead, and hydrogen sulphide, reduced Fehling's solution about five-eighths as strongly as glucose. This result is however not different from that obtainable from any plant juice which contains sucrose mixed with invert sugar.

Again, after crystals of the sugar had been obtained, they were inverted by heating with 10-per cent. hydrochloric acid at the boiling-point for some time, and the specific rotation was observed to be $(\alpha)j = -14.39°$ to $14.53°$. But these are numbers which might easily result from the inversion of pure sucrose under the given conditions since, as is well known,

levulose is rapidly destroyed by hydrochloric acid at 100°, and the rotatory power of invert sugar correspondingly lowered, so that the accepted method for inversion of sucrose employs very dilute acid and a temperature of 65°.

In watery solution the agavose dissolved calcium oxide which was again precipitated by alcohol or by a current of carbon dioxide. This is also a property of sucrose.

But while the characteristics of agavose thus far described might be explained on the assumption that the juices of the agave contained a mixture of invert and cane-sugar, the optical inactivity of the agavose is not to be accounted for on any such grounds. A new sugar of so abundant occurrence as that of the agave and with the properties described, would be an important and interesting addition to the list of carbohydrates. An opportunity was therefore sought to secure a specimen of agavose in order to verify the properties ascribed to it by Michaud and Tristan as well as to study it farther.

We have obtained two specimens of the juices of the *Agave Americana* collected at different times, for both of which we are indebted to Senor Manuel Guillen, of Mexico City, an extensive cultivator of the agave and producer of the "pulque" or fermented product of its juices. Senor Guillen, acting under directions from us, collected the fresh juices of the stalks of the agave plant, which were immediately evaporated in porcelain to a thick sirup and expressed to us in sealed bottles. Each of us has taken one of these samples which, it will be noted, contained the entire constituents of the juice of the agave, and, working separately, has isolated the sugar contained in it, and determined the characteristics of the same. Our results are given separately although practically identical with each other.

Sample A.—Received in June. The sirup on arrival contained a mass of large and well-developed crystals. The uncrystallized portion reduced Fehling's solution strongly. Of this specimen only the crystals which had formed on arrival were examined. They were separated from the sirup, and washed with dilute alcohol. They were nearly colorless, and had the characteristic appearance of sucrose crystals. After crushing and washing with alcohol the material was snow-white with a pure sweet taste. Examination showed:

1. The sugar was without effect upon Fehling's solution, but after warming with a few drops of acid it acquired a strong reducing power.

2. In 10-per cent. solution the sugar had a specific rotation $(\alpha)_D = 65.5°$.

3. After inversion by warming with very dilute hydrochloric acid for thirty minutes at 65° the specific rotation was $(\alpha)_D = -20.1°$.

4. The melting-point taken without special care in previously drying the material, was found to be 179°.

These results indicate plainly that the sugar under examination was sucrose.

Sample B.—Received in August. The material was a clear, brown sirup, free from crystals, but reducing Fehling's solution strongly. Upon concentration, the sirup crystallized and yielded upwards of 80 grams of brownish-colored crystals. These crude crystals, even after washing with alcohol, still contained enough of invert sugar to appreciably reduce Fehling's solution. The sirup was carefully concentrated until the last traces of crystallizable sugar had been separated. The residue was small in amount, reduced Fehling's solution strongly, and had a disagreeable taste, as might be expected from the presence in concentrated form of all the non-crystallizable constituents of the agave juice.

The different portions of crystals were united and recrystallized several times from both alcohol and water, care being taken to save all mother-liquors and washings. The final product was snow-white and finely crystalline, easily soluble in water, insoluble in strong alcohol at ordinary temperature, and very sweet. The material was systematically examined by all the well-known tests for identity, with the following results:

1. Specific rotation. In a 10-per cent. watery solution, the specific rotation was observed to be $(\alpha)_D = 66.3°$.

2. Action on Fehling's solution. No reducing effect was observed beyond the slight action always noted when sucrose is boiled for some time with Fehling's solution and not exceeding that produced in a check-test with pure sucrose.

3. Melting-point. A test with samples crystallized from both water and alcohol checked against a sample of pure sucrose, gave in all three cases 183° to 184°.

4. When subjected to the action of ordinary yeast, fermentation was rapid and complete.

5. For a study of the behavior of the sugar by inversion, 2 grams of the material were dissolved in about 35 cc. of water to which was added 1 cc. of strong hydrochloric acid. The solution was kept in a water-bath at from 60° to 65° for thirty minutes, and was then neutralized with soda and filled up to a volume of 50 cc. The specific rotation was found to be $(\alpha)_D = -20.6°$.

6. The reducing power of the invert sugar was determined by titrating the same into undiluted Fehling's solution and it was found that 4.94 mgms. of the invert sugar were necessary to reduce the copper in 1 cc. of Fehling's solution.

7. The phenylhydrazine compound prepared from this invert sugar melted at 203°.

8. The sugar when warmed with sulphuric acid, was immediately blackened and charred. Heated in solution with caustic soda it gave no brown coloration.

9. When warmed in solution with α-naphthol and strong hydrochloric acid a deep purple color resulted; with resorcin and hydrochloric acid, a cherry-red color.

It is apparent that the results of all these tests correspond strictly with the properties ascribed to sucrose, and that the results of two observers from two separate specimens are identical. The sugar thus studied is the only crystallizable sugar occurring in appreciable quantity in the juices of the *Agave Americana*. The possibility of any other sugar being present, aside from the invert sugar noted in the uncrystallizable portion of the sirup, is very remote. Messrs. Michaud and Tristan mention the occurrence of no other sugar save that which they describe as agavose, and there is no doubt that we have studied the same sugar as they, possibly in a purer state. That this sugar is sucrose seems also to be proved beyond doubt. For the present, therefore, the supposed new sugar, agavose, would seem to be a case of mistaken identity.

THE LAW OF MASS ACTION.

By J. E. Trevor.

Van't Hoff's famous derivation of the law of mass action from the principles of thermodynamics,[1] is essentially simple in character, but it involves an amount of machinery in the way of cylinders, pistons, and reservoirs, which is frequently found embarrassing when the subject is approached for the first time. The modification of this proof, which has been adopted by Nernst,[2] suffers from a similar disadvantage, and it requires, in some cases, the removal of a dissociating substance in undissociated form, thereby necessitating quite undue haste in the imagined experimentation. And both forms of the proof introduce the not entirely satisfactory feature of a completely semi-permeable wall, which can be employed in all cases.

It would seem, therefore, not undesirable that the demonstration in question should be brought into a more simple and a more general form; although this must be done in the interest of simplicity of statement and not at all with the intention to cast discredit upon an idea which bears distinctly the mark of genius.

The law of mass action has hitherto found application only in the limiting case when the energy of the substances participating in a transformation is practically independent of their volume; that is to say, when these (gaseous or dissolved) substances are relatively dilute. In such cases the free energy of a change in concentration is proportional to the absolute temperature at which the change occurs, and the well-known relation

$$pv = RT \qquad (a)$$

follows. The letters denote successively the actual pressure, the molecular volume, the gas-constant, and the absolute temperature.

Let us consider a chemical equilibrium established between the initial components A_1, A_2, etc., and the products a_1, a_2, etc., which they unite to form; the law (a) to hold for all constituents, and the equilibrium to be represented by the chemical equation

$$N_1A_1 + \ldots = n_1a_1 + \ldots$$

[1] Ztschr. phys. Chem., 1, 498 (1887). [2] Theoretische Chemie, 510.

At equilibrium the free energy F developable by this system must be a maximum, so for a virtual displacement in the positive direction of change

$$\delta F = 0$$

$$\delta F \equiv \Sigma n.v\delta p - \Sigma NV.\delta P = 0, \qquad (1)$$

the two terms of the left-hand member of the equation being summated over all the initial components (capitals) and their products (small letters) respectively. The concentration relations which obtain at the equilibrium are sought; so the above differentials of the elastic energies of the reacting components must be expressed in terms of the respective molecular concentrations, which can be done with the aid of the governing relation $pv = RT$ between pressure and concentration.[1] The substitution yields

$$\delta F \equiv RT(\Sigma n\delta \log c - \Sigma N\delta \log C) = 0. \qquad (2)$$

These values of c and C are the molecular concentrations in the state of equilibrium.

The work-value of the process, the limiting value of F for the change considered as occurring isothermally at its equilibrium, is obtained by integration of this virtual change over the entire transformation of n_1, etc., mols,

$$F = RT\int(\Sigma\partial \log c^n - \Sigma\partial \log C^N) \qquad (3)$$

the constant of integration disappearing from the definite integral. This becomes

$$F = RT \log K \qquad (4)$$

when the change is conducted in the positive direction and K is set for the ratio $\Pi c^n/\Pi C^N$. And since F must be constant for a given isothermal change this ratio must be constant also, —which is the law of mass action.

The value (4) of the chemical affinity F must be clearly distinguished from the actual free energy Φ developed by the process when the initial state includes none of the products of the reaction. Φ is the free energy of the change as it actually

[1] In this process we eliminate $v = RT/p$ and set dc for the dp, to which it is proportional; or we eliminate $dp = -(RT/v^2)dv$ and replace the molecular volume by its reciprocal, the molecular concentration; or we write (1) as $\delta F \equiv \Sigma N.P\delta V - \Sigma n.p\delta v$ and eliminate $p = RT/v$, replacing v by $1/c$; or eliminate $dv = -(RT/p^2)dp$, replacing dp by dc. The transformation is the same in each case, except that in the first and last modes the condition of constant temperature is introduced. The writer prefers the third mode.

occurs, while F is the limiting value obtaining at equilibrium; Φ is the affinity to which the formation of the resultant mixture of substances is due; F is the affinity which the two reacting systems have for each other in this mixture.

The disturbing influences of variations in temperature are then pursued in the usual way, by partial differentiation of (4) to obtain

$$RT.\frac{\partial \log K}{\partial T} = \frac{-E}{T};$$

$-E$ signifies the energy difference of the two reacting states.

CORNELL UNIVERSITY, *January*, 1895.

CHROMATES OF THE RARE EARTHS: CHROMATES OF THORIUM.[1]

BY CHASE PALMER.

Believing that a study of the action of an acid of feeble energy upon the weak bases of the tin group—or Fourth Group of Mendeléeff's Periodic System—would throw new light upon this interesting family of elements, I have undertaken a comparative study of the action of chromic acid upon the oxides of the rarer metals of this group, and of the conduct of their salts towards the alkaline chromates.

The chromates of the rare elements of this group have hitherto received but little attention from chemists. The earliest allusion to a chromate of a rare earth was made in 1863 by J. J. Chydenius.[2] This author observes that thorium hydroxide is soluble in chromic acid. He states that from the resulting solution, evaporated over sulphuric acid, he obtained normal thorium chromate as a soluble salt containing 8 molecules of water of crystallization. Chydenius further states that potassium dichromate produces no precipitate when added to a solution of thorium chloride, until after the mixture is neutralized with ammonia, whereby a basic salt of thorium is thrown down. The only other allusion to a chromate of a rare metal of the Fourth Group, in the literature accessible to me, is made by Pattison and Clarke.[3]

[1] I wish to express here my hearty thanks to Professor Edgar F. Smith, through whose generous hospitality I have enjoyed the facilities of the John Harrison Chemical Laboratory of the University of Pennsylvania, where the work described in this paper has been done.

[2] "*Thorerde und deren Verbindungen*:" Ann. der Phys. Pogg., **119**, 43.

[3] Chem. News, **16**, 259.

These chemists observed that by heating the residue from an evaporated solution of the hydroxides of cerium, lanthanum, and didymium in chromic acid, the cerium compound was rendered insoluble; but there is no evidence that they determined the composition of the insoluble product.

Thorium was chosen as the first element for the present research on account of the highly developed basic properties of its oxide. Contrary to the observations of Chydenius, I have found, not only that a difficultly soluble salt, having the composition of normal thorium chromate, separates spontaneously from a solution of thorium hydroxide in chromic acid, but also that the same compound is precipitated by potassium dichromate from thorium nitrate without the aid of a neutralizing alkali. I have also found that potassium chromate produces the same compound indirectly from a soluble thorium salt.

Thorium Hydroxide and Chromic Acid.—Pure, freshly precipitated thorium hydroxide was added in portions to a solution of pure chromium trioxide in water. The quantity of the trioxide was slightly in excess of the amount required to form the normal chromate. The hydroxide was quickly dissolved at first, but afterwards the acid attacked it more sluggishly. A flocculent orange precipitate soon appeared, and finally settled as a fine powder. Under the microscope this product shows a crystalline structure. The formation of the orange precipitate takes place more quickly at 90° C. than at the ordinary temperature.

Dried at 120° C. to constant weight the product was analyzed:

0.2016 gram substance at 180° lost 0.0072 gram H_2O and gave 0.1114 gram ThO_2 and 0.0626 gram Cr_2O_3.

	Calculated for $Th(CrO_4)_2.H_2O$.	Found.
H_2O	3.73	3.57
Th.....	48.05	48.55
Cr.....	21.71	21.29

Thorium Chromate from Chromic Acid Solution.—Pure, freshly precipitated thorium hydroxide, in small portions at a time, was stirred in a cold solution of chromic acid as long as

it was taken up. At the first appearance of the orange precipitate, the latter was filtered off, and the solution evaporated over sulphuric acid *in vacuo*. From the concentrated solution thorium chromate separated out in orange-colored scales containing 2 molecules of water of crystallization and 1 molecule of water of constitution.

Dried to constant weight over sulphuric acid the salt was analyzed:

I. 0.215 gram substance lost 0.0148 gram H_2O at 120°; at 180° it lost 0.007 gram H_2O additional, and gave 0.1104 gram ThO_2 and 0.0631 gram Cr_2O_3.

II. 0.2155 gram substance lost 0.015 gram H_2O at 120°; at 180° it lost 0.0068 gram H_2O additional, and gave 0.111 gram ThO_2 and 0.0622 gram Cr_2O_3.

	Calculated for $Th(CrO_4)_2 \cdot 3H_2O$.	Found. I.	II.
$2H_2O$	6.90	6.88	6.96
H_2O	3.46	3.25	3.15
Th	44.71	45.12	45.26
Cr	20.20	20.12	19.70

Thorium Nitrate and Potassium Dichromate.—On mixing the boiling solutions of these salts in the proportion of 1 molecule of the nitrate to 2 molecules of the dichromate, hydrated thorium chromate was precipitated at once as a fine orange powder. In this way 78 per cent. of the theoretical yield was obtained.

0.1986 gram substance, dried at 120°, lost 0.0073 gram H_2O at 180° and gave 0.1095 gram ThO_2 and 0.0068 gram Cr_2O_3.

	Found.
H_2O	3.67
Th	48.35
Cr	21.34

When the cold solutions of thorium nitrate and potassium dichromate were mixed no immediate precipitation occurred, but in a short time a precipitate began to form. After standing twenty-four hours the orange precipitate that had formed meanwhile was filtered off, washed, and dried at 120°.

0.1817 gram substance lost 0.0064 gram H_2O at 180°, and gave 0.1008 gram ThO_2 and 0.0569 gram Cr_2O_3.

	Found.
H_2O	3.52
Th	48.75
Cr	21.47

The filtrate from this precipitate was heated to 90°. At 60° a second precipitation of the thorium chromate occurred. The first yield was 65 per cent., and 14 per cent. additional was obtained by heating the filtrate. The total yield (79 per cent.) closely corresponds with the yield obtained by precipitating the compound at once from a boiling solution.

The mother-liquor from the second precipitate was reduced to small volume, but no further precipitation occurred. By evaporating it to dryness a very soluble crystalline product was left, but it could not be isolated for examination.

Thorium Nitrate and Potassium Chromate.

There are two stages in the formation of hydrated thorium chromate from thorium nitrate and potassium chromate. When a solution of thorium nitrate is treated with a solution of potassium chromate (one molecule of the former to three molecules of the latter) the precipitate, which at once forms, dissolves immediately until the mixture is complete. Then a dense golden-yellow precipitate separates from the solution. The liquid meanwhile becomes red, owing to the formation of potassium dichromate. By promptly removing the yellow precipitate from contact with the fluid it was found, on analysis, to be basic thorium chromate.

0.2367 gram substance dried at 100° gave 0.1635 gram ThO_2 and 0.0459 gram Cr_2O_3.

	Calculated for $Th(OH)_2CrO_4$.	Found.
Th	60.66	60.70
Cr	13.70	13.29

If the basic thorium chromate be allowed to remain in contact with the supernatant liquid, it is gradually changed into the orange precipitate which, upon analysis, proved itself to be the same hydrated thorium chromate already described. During this transformation the red liquid is changed to the bright yellow color of potassium chromate.

Analysis of the final product dried at 120°.

0.2136 gram substance at 180° lost 0.0081 gram H_2O and gave 0.1175 gram ThO_2 and 0.0678 gram Cr_2O_3.

	Found.
H_2O	3.79
Th	48.34
Cr	21.77

The complete reaction may be expressed by the two equations:

1. $Th(NO_3)_4 + 3K_2CrO_4 + H_2O = Th(OH)_2CrO_4 + K_2Cr_2O_7 + 4KNO_3$;
2. $Th(OH)_2CrO_4 + K_2Cr_2O_7 = Th(CrO_4)_2.H_2O + K_2CrO_4$.

The hydrated thorium chromate always has a full orange color, which it does not lose even after prolonged heating at 130°. The color of the anhydrous salt is ochreous yellow. At 22°, 1 part of the salt is soluble in 284 parts of water. It is readily soluble in hydrochloric acid and in ammonium carbonate. At a dull red heat it is decomposed into thorium dioxide and chromic oxide. Heated in a platinum crucible over a Bunsen lamp the substance lost 10.41 per cent. in weight. For the loss of three oxygen atoms to form ThO_2 and Cr_2O_3 the required loss in weight is 10.32 per cent.

Constitution of the Orange Chromate.—It is noteworthy that the orange chromate of thorium always contains one molecule of firmly bound water, whether the substance be formed by slow crystallization from a chromic-acid solution, or by precipitation from a soluble salt, or formed from the insoluble basic chromate. The substance may be regarded simply as hydrated normal thorium chromate ($Th(CrO_4)_2H_2O$), or it may be a basic dichromate of thorium having the constitution expressed by the formula $Th\begin{matrix}\swarrow Cr_2O_7 \\ \searrow (OH)_2\end{matrix}$.

Before expressing an opinion as to the more probable constitution of the orange chromate, I shall attempt to gather more knowledge of these chromates and of the compounds of chromic acid with the related elements.

Zirconium hydroxide is attacked by chromic acid less readily than is thorium hydroxide. It can be completely dissolved in an excess of the acid. A yellow precipitate was obtained

by boiling this solution. From an analysis, the product appears to be a basic salt.

A similar yellow precipitate is obtained by the action of potassium dichromate on zirconium chloride. The precipitate, dried over sulphuric acid, gave 41.24 per cent. Zr and 16.38 per cent. Cr. It is probably a basic salt.

I intend to make a thorough study of the chromates of zirconium and of the other elements of the Fourth Group.

ON A NEW METHOD FOR THE SEPARATION OF COPPER AND CADMIUM IN QUALITATIVE ANALYSIS.

By Allerton S. Cushman.

The successful separation of small quantities of cadmium from copper has been one of the difficult operations of qualitative analysis. The method depending upon the solubility of copper sulphide in potassium cyanide, is not considered by most chemists so desirable as the method of boiling the mixed sulphides in dilute sulphuric acid, on account both of its inferior delicacy, and of the unpleasant character of the reagent. The last edition of Crookes' "Select Methods in Chemical Analysis," has to say on this subject: "Cadmium sulphide dissolves with the greatest facility in boiling dilute sulphuric acid, which has no action on copper sulphide. On precipitating, by sulphuretted hydrogen, a solution containing not more than 1 milligram of cadmium mixed with 1000 milligrams of copper and boiling the black precipitate for a few seconds with dilute sulphuric acid (1 part concentrated acid and 5 parts of water), a colorless filtrate is obtained in which an aqueous solution of sulphuretted hydrogen produces an unmistakeable precipitate of yellow cadmium sulphide. Another solution of the same composition was mixed with an excess of potassium cyanide and treated with sulphuretted hydrogen gas. A distinct yellow coloration was observed; a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in potassium cyanide also gives rise to a yellow coloration when submitted to the action of sulphuretted hydrogen."

Undoubtedly the sulphuric-acid separation is an exceedingly delicate one, when performed under the conditions detailed in the foregoing. When, however, the amount of copper present is large, and the filtration of the mixed sulphides is prolonged, traces of copper are almost certain to find their way by oxidation into the sulphuric-acid solution, in which case, on addition of hydrogen sulphide, the yellow color of the cadmium sulphide is invariably masked by the brown tinge of the sulphide of copper. Very small quantities of cadmium dissolved in an excess of dilute sulphuric acid may very easily escape detection on further dilution and addition of hydrogen sulphide unless extreme care, cleanliness, and rapidity in filtration have been observed. Certainly few metals oftener escape detection in elementary practice than does cadmium when present in small quantity with copper.

In the solutions that were given out for analysis to the students in this laboratory, it was noticed that when cadmium and antimony were present in the same solution, the cadmium frequently failed to be precipitated by hydrogen sulphide out of acid solution, but made its appearance with the precipitates of Groups III–IV. It seemed that the only explanation of this lay in the fact that a strong solution of sodium chloride had been added to each mixture in which antimony was put, in order to prevent the separation of basic compounds of the latter metal. In the course of an investigation bearing upon this subject, it was found that when cadmium sulphide was treated with a saturated solution of one of the alkaline chlorides in the presence of dilute hydrochloric acid, it immediately dissolved to a clear solution with evolution of hydrogen sulphide. As far as can be learned this reaction between cadmium sulphide and solutions of the alkaline chlorides in the presence of dilute hydrochloric acid has been nowhere noted. The ability of the alkaline chlorides to form double salts with many of the metals is well known, and according to V. Hauer, cadmium chloride unites with the alkaline chlorides and chlorides of the alkaline earths to form compounds of the general formulae: $4RCl,CdCl_2$; $2RCl,CdCl_2$; $RCl,CdCl_2$.[1] On boiling cadmium oxide and cadmium car-

[1] Pharm. Centralbl., 1858, 292, 787; 1856, 766.

bonate with ammonium chloride solution a double crystalline compound has been obtained with the formula $2NH_4Cl$, $2CdCl_2, H_2O$.[1]

In order to see if a strong neutral solution of ammonium chloride had any action on cadmium sulphide the following experiment was made: A solution of cadmium nitrate was precipitated by hydrogen sulphide, and the precipitate thoroughly washed by decantation with boiling water until free from last traces of sulphuretted hydrogen. The precipitate was then thrown on a filter, sucked dry, and finally dried at 100°. A quantity of this dried cadmium sulphide was suspended in a concentrated solution of ammonium chloride in a flask which was connected with a Varrentrapp-Will tube containing a solution of lead acetate. The temperature of the mixture was then gradually raised without producing any precipitate in the bulb-tube until protracted boiling had taken place, when a decided precipitate of lead sulphide appeared in the tube. It is a well-known fact that solutions of ammonium chloride become acid on prolonged boiling owing to dissociation and escape of ammonia.[2] As the partial reaction in this case only began after prolonged boiling it is probable that it was due to the formation of free hydrochloric acid in the solution. On addition of dilute hydrochloric acid to the mixture in the flask, the cadmium sulphide immediately dissolved. On repeating the foregoing experiment using sodium chloride instead of ammonium chloride, no hydrogen sulphide was given off except in the presence of free hydrochloric acid. In a general way the reaction is perhaps best expressed by the following: $CdS + 2RCl + 2HCl = CdCl_2, 2RCl + H_2S$.

This solubility of cadmium sulphide in acidified concentrated solutions of the alkaline chlorides, renders possible an exceedingly delicate method of testing for cadmium. If to 2 cc. of a solution containing a small amount of cadmium, 10 cc. of a saturated solution of salt and a few drops of dilute hydrochloric acid be added, hydrogen sulphide fails to produce any precipitation even up to saturation of the liquid by the gas. If now a few drops of dilute ammonia be allowed to flow down

[1] Graham Otto, Aufl. 5, III., 828.
[2] Ann. Chem. (Liebig), **128**, 189; Graham Otto, III, 485.

the side of the tube a distinct yellow ring or layer of cadmium sulphide appears at the junction of the two liquids. By this method 1 cc. of a solution containing 0.1 milligram of cadmium sulphate developed a distinct yellow ring in a few minutes, while three drops of the same solution, equal to an amount less than 0.01 milligram of cadmium, developed a perceptible ring on standing half an hour.

The fact that copper sulphide has been found quite insoluble in the reagents, offers an easy and delicate method of separating the two metals. When the metals are present in comparatively large quantity it is only necessary to treat the mixed sulphides with an excess of a strong solution of salt and a little dilute hydrochloric acid, when, on warming, the cadmium sulphide entirely dissolves. On dilution of the filtrate and addition of hydrogen sulphide, the cadmium sulphide is re-precipitated. The method is more accurately carried out in this laboratory as follows: About 2 cc. of the solution containing the two metals is made slightly acid with hydrochloric acid and about 20 cc. of a saturated salt-solution added, the solution warmed, and hydrogen sulphide passed through until the copper is all precipitated and the hydrogen sulphide is present in excess. The copper sulphide is then filtered off through a dry filter, and the filtrate run into a dry test-tube. The filtrate collected in the tube should be perfectly clear, as the slightest dilution begins to precipitate the cadmium. Therefore if a few drops of water be allowed to run down the side of the test-tube, a yellow line will be formed at the junction of the two liquids if cadmium is present. Diluted ammonia may be substituted for water with advantage if the amount of cadmium present is very small, as it develops the yellow layer more rapidly than water does. On the other hand if traces of other metals are present through incomplete removal in the group separations, the result will be obscured by the use of ammonia.

This method has been thoroughly tested with mixtures of solutions of copper and cadmium in varying proportions, and has been found extremely sensitive. Sometimes it has been found that, when very minute quantities of copper are present, the copper sulphide is precipitated in the strong solution of

sodium chloride in so finely divided a condition that it is impossible to remove it completely by filtration. In this case the addition of a few drops of a solution of copper sulphate, and re-precipitation with hydrogen sulphide obviates the difficulty.

In the hands of students the method has given uniformly good results when carried out with the ordinary care necessary to the success of all analytical processes. As some other metallic sulphides, notably those of lead and bismuth, are found to be soluble in strong acidified solutions of the alkaline chlorides, these metals must be as completely removed as in any other test for cadmium.

The bearing of these reactions with lead, bismuth, and cadmium sulphides on qualitative and quantitative separations, will be more fully studied in this laboratory in the future. The simplicity of the reagents used, and the delicacy of the test for cadmium will probably commend the method to chemists and instructors in qualitative analysis.

ST. LOUIS, MO., Feb. 27, 1895.

REVIEWS.

GERMAN OFFICIAL REPORT ON CHEMICAL INDUSTRY AT THE CHICAGO EXHIBITION OF 1893. Dr. OTTO N. WITT. Die chemische Industrie auf der Weltausstellung zu Chicago, und in den Vereinigten-Staaten von Nord-Amerika, in 1893. Berlin, 1894.

The author of this report, who is Professor of Chemical Technology at the Royal Technical High School of Berlin, in his visit to the United States in the summer and autumn of 1893, set before himself two objects—a study of the products of chemical industry exhibited at Chicago, and an examination of the present state and future prospects of chemical manufactures in this country.

While acknowledging with gratitude the obliging readiness of individual exhibitors, and of those connected with American manufacturing establishments, to afford information, he makes more than one significant allusion to defects of management which marred the Chicago exhibition for thoughtful students of it as a serious display of the world's work—the imperfection with which much of the pretentious plan was carried out, the difficulty of finding many things scattered among the huge buildings, the uselessness of the official general catalogue, the poor light in large portions of the space devoted to

exhibits, etc., etc. He found but three countries at all worthily represented in the field of chemical industry—namely Germany, the United States, and Japan—and felt most interest in the contrast presented by his own country, of originally limited resources, but now possessing the most highly developed chemical manufactures, with the United States, gifted by nature with resources in the way of raw material wonderful in extent and variety, but barely beginning to develop and utilize them.

Some very important branches of industry dependent upon chemical principles, including some that have become well established in this country and owe much in the way of improvement to American skill and enterprise, are excluded from consideration in the report. Thus metallurgical processes, and all those processes more or less closely connected with food, such as the preparation of sugar and starch, brewing, distilling, etc., are omitted. The subject is treated under three main heads—fuel, inorganic chemical products, and chemical products of organic origin or character.

Under the first head there is a condensed account of American petroleum, its varieties, distribution, extraction, and refining, including some comparison with the treatment of the analogous Russian product, and some notice of its special value as heat-producing fuel in certain manufacturing operations. Attention is drawn to the mineral oil distilled at Sydney from the bituminous shale of New South Wales, this shale being reported as existing on quite a large scale.

In noticing the abundance of coal in the United States and its immense importance for the future, with which the author was greatly impressed, he finds it least troublesome to mention the States only (9 in number) in which workable coal has *not* been found. He observes the less depth of most American coal mines than of those in Europe, and hence in part the superior cheapness of the product—also the freer choice between anthracite and bituminous coal over a large part of the country. He comments on the occurrence of the most valuable coal beds in the regions comparatively near the Atlantic coast, while the coal of the interior of the continent is for the most part of more recent age and poorer in quality, and concludes from this difference that to the Atlantic States belongs, in the main, the future of chemical manufacturing on the great scale. He did not see any sign of efforts to secure smoke consumption, and was surprised to find so little progress toward saving the by-products (tar and ammoniacal liquor) of coking bituminous coal, as is now quite successfully done in the Rhenish provinces and in Silesia. He understands that the great extension of electric lighting, and the general use in the larger

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cities of the United States of "water-gas"[1] instead of coal-gas proper for illuminating purposes, offer little prospect of tar and ammonia products growing in importance in the future, although the Solvay-process soda-works at Syracuse, N. Y., have started an experimental set of Semet-Solvay coke ovens, saving the by-products. Hence the outlook for American competition in the multifarious chemical industries based upon the constituents of tar does not at all alarm the German observer. It would seem, however, that the enormous demand in this country for fertilizers of all kinds, including the nitrogenous, ought to lead the managers of the great Pennsylvanian and West Virginian coke works to look carefully into this question of saving the by-products obtainable by some of the more modern types of ovens. If the day has not yet come, or perhaps may never come, for rivalling here the great German factories for coal-tar colors, medicinal agents, artificial perfumes, etc., it does not seem certain that crude benzene, toluene, anthracene, phenol, and the like, might not be made with profit on a large scale in America, by first distillation of tar, if the tar itself were saved in adequate quantity to build up a large business.

The reporter comments, as so many others have done before him, on the reckless destruction of wood in the great forest-covered regions of the United States. He notes the fact that the dry distillation of wood, yielding acetic acid, methyl alcohol, and acetone, is carried on in this country; but this industry was not represented at the Chicago exhibition, and he apparently did not hear of some interesting peculiarities which American works have developed in connection with it.

As respects the prime natural materials for chemical industry on the great scale, Dr. Witt does not consider the United States so highly favored as Europe. He notes the fact that this country is now the greatest consumer of sulphur (as such) in the world, pointing out that in 1889 there was imported from Sicily three times as much as was taken by England in the same year, some moderate amount coming in from Japan at San Francisco, a few hundred tons only of domestic sulphur being supplied by California, Nevada, and Utah, and none yet furnished by the great Louisiana bed in Calcasieu Parish, which is so far known only by borings. The reporter seems to look for little increase in the use of pyrites for making sulphuric acid, observing that only Massachusetts and Virginia furnish pyrites in any important quantity, but on this point he probably underrates the influence of present commercial conditions favoring the use of native sulphur, and the pos-

[1] The reporter is severe in his allusion, later on, to the recklessness with which illuminating gas of such highly poisonous character is admitted to dwellings in America.

sibilities of the future in the way of larger supply of pyrites (as from Georgia, New York, and some of the Western States) under the stimulus of increased demand. He not unnaturally speaks of rock salt in the United States as a small affair in comparison with the vast European deposits at Stassfurt, Wieliczka, etc., but hardly does justice to the extent of production of American boiled salt for the country at large, though he describes with interest the many square miles of shallow wooden tanks at Syracuse for evaporation of brine at atmospheric temperature, and notices the exhibit at Chicago of boiled salt from the Great Salt Lake of Utah. Mention is made of "*Abraumsalz*" (Kainite) as shown from the Louisiana salt bed on Petit Anse island, but it may be questioned whether there was not some mistake about this. It is conceded that American limestone is abundant and widely distributed. Manganese ore is said to be chiefly used in this country for decolorizing glass, but this statement seems to ignore the great scale on which it is now called for by the large steel works. It is stated that large quantities of oxide of manganese in the form of "Weldon mud" are imported into the United States and used in coloring tiles and terra-cotta blocks in imitation of, or to harmonize with, "brownstone." Notice is taken of the native carbonate and sulphate of soda from Wyoming as interesting American specialties. The only worthy exhibits of crude chemical materials from Europe were those of English salt and German (Stassfurt) potash and magnesia compounds.

There was practically no general display at Chicago illustrative of the production of acids and alkalies on the great scale. Notice is taken of the extensive use in America of Sicilian and "regenerated" sulphur for making sulphuric acid, and the consequent greater freedom of the acid than in Europe from arsenic, making easier the production of pure hydrochloric and nitric acids. The great demand now for bicarbonate of soda, growing out of the widespread use of "baking powders" and the large consumption of soda-water, and the more frequent use than in Europe of carbonate of soda instead of sulphate of soda for glass-making, are facts shown to bear strongly on the question of the alkali industry becoming established on a great scale in America. Few facts in regard to chemical manufactures are more remarkable than that this has not yet taken place. Notice is taken of the ammonia-soda works at Syracuse, N. Y., operating under the Solvay patents, but making no separate exhibit of the product, which was shown in the French department, and very favorable comment is made on the cryolite-soda works of Natrona, Pa., the special *raison d'être* for which is taken to be the large demand in the United States for aluminium salts for

paper-making, dyeing, etc., with relative scarcity of bauxite; the Natrona establishment is spoken of as a good example, "the only one in America," of an undertaking in the way of large chemical manufacture well devised to meet actual conditions, complete in itself, and working up all by-products. Dr. Witt does not seem to have heard of the large alkali works which are being built at Saltville in South-western Virginia, at which it is proposed to operate on both the Leblanc and the ammonia-soda plans. An extended account is given of the exhibit made at Chicago in the English section by the great "syndicate," (formed in 1890), known as the United Alkali Co., the largest joint stock chemical manufacturing company in the world, with a total capital of nearly £9,000,000 sterling, uniting 45 great chemical factories, 3 salt works, 2 soap factories, and 1 rosin refinery. Attention is drawn to several of the special products of this company, such as the very convenient caustic soda *in powder* (pulverized in closed mills, excluding the air), the "crystal carbonate of soda" (crystallized hot, with but a single molecule of water of crystallization) which has the advantage over ordinary soda crystals of greater concentration and offers an equal guarantee of purity, the sodium chlorate (with greater solubility than that of potassium chlorate) for print works, the barium chlorate giving aniline chlorate by interaction with aniline sulphate, the sodium manganate for use as a cheap disinfecting material, the finely pulverulent chromium trioxide in air-tight packages for Bunsen batteries, and the regenerated sulphur from the Leblanc process, of which 40,000 or 50,000 tons a year are produced, much of which finds a market in the United States to be again converted into sulphuric acid.

Ammonia-soda appeared at the exhibition not only from the Solvay works in France (*Varangéville-Dombasle*), but from English and Russian establishments.

Under the head of materials used as manures it is remarked that Germany holds essentially a monopoly of potash salts; that the United States depends for nitrogenous material upon South American nitrate of soda and European sulphate of ammonia, neglecting the advantages offered by modern coke ovens for saving the nitrogen of coal, but that to this country must be conceded the first place in the supply of phosphates. The reporter fully recognizes the great importance of the phosphate deposits of South Carolina and Florida, especially the latter, which he visited and gives some description of.

The extent and importance of the American manufacture of glass are noted, though this industry was very poorly represented at Chicago. The reporter was impressed by the good results of using (since 1880) furnaces fired with natural gas, and also with artificially prepared gaseous fuel ("generator"

gas), the high and easily controlled temperature of these furnaces having regenerative chambers on the Siemens principle being very advantageous. The development in this country of the manufacture of *pressed* glass is favorably noticed. The great European glass works were unrepresented at the Chicago exhibition, with the exception of a handsome display of Bohemian ornamental glassware. Notice is taken of the important improvements made of late in Germany in the composition of glass for various scientific purposes, the Jena glass for optical instruments, for thermometers, and for chemical laboratory vessels (resisting ordinary liquid reagents to a remarkable extent)—and it is observed that Japan for the first time sent forth glass of her own manufacture.

Clay-ware was much better shown than glass at Chicago, and the reporter seems to have felt especial interest in the details of some of the methods by which more or less new results were obtained. Mention is made of a new porcelain-ware introduced at the Royal Porcelain Factory of Berlin, which is very refractory and becomes, not denser, but more porous in the firing—valuable for removal by filtering of bacteria from water, for porous diaphragms in electrolysis, etc. There is an interesting account of Japanese clay work, including mention of "*Kaga*" (hard porcelain) figures formed, not in molds, but by free-hand sculptor's modeling. In connection with the chemistry of clay-ware, the extensive use in the United States of Weldon mud for coloring terra-cotta, and the free addition of precipitated barium carbonate to prevent efflorescence, receive notice.

Under the head of chemical apparatus and appliances, the very handsome displays made by Herœus of Hanau, and Johnson and Matthey of London, of platinum apparatus, the rare platinum metals and their salts, etc., are spoken of with deserved admiration.

Among the smaller and finer products of chemical manufacture the two most interesting novelties noticed were both American; *viz.*, the oxides and salts of the rare earthy metals, thorium, zirconium, yttrium, lanthanum, etc., prepared from North Carolina monazite, zircon, etc., and used by the Welsbach incandescent gas-light company, in regard to which it is noted that the higher temperature afforded by "natural gas" gives a better light from the wicks made by skeletons of these metallic oxides than when artificial "water-gas" is used,—and the new carbide of silicon, or "carborundum" made by Acheson, of Pennsylvania, from sand, coke, and a little common salt intensely heated in an electric furnace. As to the value as an abrasive of this material the reporter states, on the authority of Dr. A. Miethe, that its effect upon glass is 9 times that of the best emery. Mixed with 30 *per cent.*

of refractory clay, carborundum is molded into cutting and polishing wheels, and burned in a small porcelain kiln. There is a rather comical notice of the wonder with which were regarded the light color and inalterability of sticks of phosphorus exhibited by J. J. Allen's Sons, of Philadelphia, explained by the fact that for safety's sake the sticks exhibited were made of paraffine! The brief mention of bromine from Pomeroy, Ohio, and of California borax, does not seem to indicate adequate appreciation of the capabilities for production of the regions in question. It is remarked, and certainly with entire justice, that by far the most extensive and complete exhibition of chemical preparations was that made by Germany—in fact no other country made anything like a worthy display. Among the novelties included in the German collection special mention is made of potassium cyanide free from cyanate, made by acting with metallic sodium on the ordinary cyanide, and intended for use in the metallurgical extraction of gold, and notice is also taken of piperazine, so highly recommended of late as a solvent for uric acid.

The reporter found at Chicago little that was new or worthy of special mention in connection with dyeing or calico-printing. He mentions with interest some Japanese ornamental work on silk, in which the effect was produced by a combination of printing and free-hand painting. This union of block and brush work is of great antiquity (upon cotton) in India. There was but a poor display of textile materials—it is observed as particularly disappointing that so insignificant an exhibit of raw cotton should have been made by the greatest cotton-producing country of the world.

The comparatively small use of candles in the United States is remarked, and the absence at the exhibition of much that was new in the manufacture of candles and soap, though there was a good deal of both products to be seen, especially of the latter. Favorable mention is made of the excellent glycerine made by Jas. S. Kirk & Co., of Chicago, from the underlye of salted-out soap, by evaporating, crystallizing out most of the salt (to be used over again), precipitating the last remains of the fatty acids in the form of insoluble salts of calcium and aluminium, and distilling the glycerine under much-reduced pressure.

As a whole the report is interesting—more so than might have been expected from the inadequate and irregular way in which the chemical products of the world's industry were exhibited at Chicago. Some new things that either have already attained importance, or seem likely to soon become important, are left without notice. Silver refining and copper refining by electrolysis are omitted, perhaps as metallurgical processes, but it is surprising to find no discussion of the

attempts being made to decompose common salt and potassium chloride by the electric current, and so to manufacture by more direct methods than those now in use, the caustic alkalies and alkaline carbonates, bleaching-powder, chlorate of potash or soda, etc. Nor is there any notice of the production in the electric furnace of calcium carbide to be used in the production of acetylene for carbureting or enriching illuminating gas (this has been going on in North Carolina for a year or two past). In the thoughtful discussion of *American* chemical industry—present and prospective—it may fairly be said that the greatest omission is that of any notice of the baneful influence in this country of *vacillation in legislation* on commercial and industrial matters. However people may differ in their views of public policy in respect to such matters, there is no room for doubt that *uncertainty* is the worst of all public enemies to industrial enterprise, and from this the United States has suffered much in the past, and seems to have little chance of exemption in the future.

J. W. M.

FRENCH OFFICIAL REPORT ON CHEMICAL INDUSTRY AT THE CHICAGO EXHIBITION. M. HALLER. Rapport du Comité 19; Produits chimiques et pharmaceutiques, matériel de la peinture, parfumerie, savounerie;—Paris, 1894.

In this report we have a view of the present condition of chemical industry, its novelties, and its prospects for the future, from a standpoint not the same with that occupied by Dr. Witt, and it presents much that is thoughtful and worthy of study.

Noticing the United States as a country of great but very imperfectly developed resources, among which he counts abundant water-power for the future extension of electrolytic processes under favorable conditions, the reporter considers Germany, England, and France as the great seats of chemical manufactures for the supply of the world at large, and contrasting the progress of these three, for the last fifteen or twenty years, he recognizes that Germany has advanced most rapidly, her gain in position being most marked within the period named, for which he examines the statistics in some detail, but dating back to the middle of the century, to the era of the birth of structural and so-called synthetic organic chemistry. He finds the causes of German success in the practical, rather than idealistic, character of the Germans, their talent for organization, and their habits of discipline, which render possible combined effort on a large scale in industrial enterprises, and in illustration he points to the value of the "Syndicate of Chemical Industry" in the united influence it has brought to

bear upon legislation as to patents and in other directions. But he lays especial stress upon the importance of German organization of scientific thought, education, and research. He is deeply impressed by the force gained from freedom in teaching, freedom in learning. He sees in the professor of a German university, not merely a medium for the transfer to pupils of already acquired information, but a former of minds and a pioneer of knowledge, a man whose best recommendation to official appointment and to promotion has been his reputation for original work, who has placed at his disposal the most ample material appliances for work, and who, as a scientific man, is more highly regarded and enjoys more social consideration in his own country than anywhere else in Europe. The writer points out the close connection established in Germany between the industrial application of scientific knowledge and the continued extension of that knowledge, so that there manufacturing chemistry, *including research*, offers a career to the scientific chemist who has been trained at a university, and quotes the fact that 4 of the largest German firms among them give constant employment to more than 230 chemists, a large proportion of whom are engaged solely in original research. German industrial success has been most conspicuous in the directions in which scientific chemistry has made most rapid progress, in organic chemistry, in the production of the coal-tar colors, of medicinally used chemicals, of artificial perfumes, of explosives.

England holds, as her main strength, to the production of the simpler mineral chemicals in gross, the manufacture of acids, alkalies (or rather alkali, since the possession of the unique Stassfurt deposits gives Germany essential control of the production of potash) and mineral salts. It is remarked that in England chemists with more or less scientific training are employed by manufacturing firms, but not to any great extent for purposes of research, and that they are, as a rule, but poorly paid. There might have been added unfavorable comment upon the ill effects of the reign of examinational cramming which has borne heavily upon English scientific education for the last quarter of a century or so, though vigorous protests against it are not lacking from some of the most competent English sources.

M. Haller, himself Director of the Chemical Institute of the Faculty of Sciences of Nancy, finds much to lament in regard to the falling back of France in the race for success in chemical industry, and in regard to the causes which seem to him to be concerned in this. He regrets the failure to revise legislation on the subject of patents since 1844, the exorbitant tax upon the alcohol which is so much needed in modern organic chemistry, but, above all, what he considers serious defects in

respect to scientific organization and scientific education. He quotes the clear-cut words of Taine on the deadening effect on higher education of the spirit of authority, and of fixed rule and programme, ending with exhaustive and exhausting examinations; the human product thus characterized: "Leur vigueur mentale a fléchi; la sève féconde est tarie; l' homme fait apparâit, et, souvent c'est l'homme fini."

Scientific education in the United States is not spoken of by the reporter at much length; probably his opportunity of examining it for himself was not very ample; but it seems to him, more than in Europe, and solely because of the conditions belonging to a new country, "d'un caractère trop positif, trop pratique, trop immédiatement utilitaire en un mot, pour qu'il puisse donner tous les fruits qu'on est en droit d'en attendre." What is said in expressing a desire for new establishments for higher scientific education in France, deserves attention in this country, that there is danger by multiplying too much such establishments of lowering the grade of instruction, and of the results attained—there is only a moderate amount of sound human material, professors and students, leaders and led, available in the country at any one time for higher education in the proper sense—and concentration of this, to a reasonable extent, is surely desirable. Those who have seen much of American educational work can hardly fail to recognize among its weak points a good-natured readiness to be not too critical, but to pass over lightly the confusion of real with self-claimed merit, and to allow every school to call itself a college, every college a university, without its being a part of anyone's business to draw over-nice distinctions on such questions. No doubt much of this will remedy itself in time, and those who can look back thirty or forty years have already seen great improvement.

Under the head of "Produits de la grande industrie chimique," the reporter has an interesting discussion of the question whether the electrolytic decomposition of common salt is soon to become the mode of utilizing its constituent elements, with both of which—sodium and chlorine—nature supplies us abundantly in but the one form of this important substance. He speculates on the profound changes which will be brought about by the industrial electrolysis of salt in the other processes of chemical industry which have hitherto been connected with and dependent on the Leblanc process. He notices the fact that already electrolytic chlorine and bleaching-powder, potassium chlorate, and caustic potash have been successfully made from the potassium chloride of Stassfurt carnallite. Notice is taken of the plan adopted at Leopoldshall for making the osmotic diaphragms of parchment-paper permanent; namely, by adding on the anode side about 2 *per cent.* of cal-

cium chloride or magnesium chloride to the brine to be electrolyzed, with the effect of forming an adherent deposit of an oxychloride of calcium or magnesium on the diaphragm, which serves to protect it. Liquefied chlorine placed upon the market in steel cylinders is mentioned as one of the newer chemical products. We have a discussion of the various attempts since 1889 (the date of the French International Exposition) to recover in useful form the chlorine of salt treated by the Solvay ammonia-soda process, with, as yet, no really satisfactory solution of the problem.

Improvements in the manufacture of sulphuric acid are limited to the means of concentrating the acid. The apparatus of Scheurer-Kestner is intended to effect a partial concentration in a platinum vessel, followed by final concentration in one of cast-iron, the transfer from the one to the other being made when the strength attained begins to entail considerable attack of the platinum and the acid ceases to appreciably act on the cast-iron. An apparatus on this principle required but 18.8 kilos of platinum, the iron part weighing 250 kilos; 4500 kilos of sulphuric acid of 95 *per cent.* could be turned out in twenty-four hours, and the loss of platinum was not more than 0.15 gram per ton of acid of 66° B. The gold-coated platinum of Heræus is mentioned, with notice of the permanent and satisfactory union of the two metals brought about by casting the gold on the surface of previously heated ingots of platinum and rolling down the compound bars so produced. The interesting proposal of Blount is not overlooked, to concentrate the acid in a glass or porcelain vessel by a platinum-wire spiral heated by the passage through it of an electric current—a wire 5 mm. in diameter and 77 cm. long, heated to 480° C. by a current of 364 amperes (at 5 volts), sufficed to concentrate 24 kilos of acid in five hours—this represents a consumption of 5 times as much fuel as would be required for direct concentration, but water-power would afford a cheaper source of power, and the quantity of platinum required is very small, while any loss from electrolytic action might, it is suggested, be avoided by using alternating currents.

The great increase of production of nitric acid, as well as sulphuric acid, of high strength, is due to the demand for the manufacture of modern explosives. At Griesheim, pure and strong nitric acid is made by condensing in a receiver kept at 80° C., beyond which is a reflux condenser; the more volatile impurities, including the lower oxides of nitrogen, are carried on.

A description is given, with a figure, of the improved form of revolving iron cylinder adopted by the Solvay firm for the heating of bicarbonate of soda made by the ammonia process

in order to convert it into the normal carbonate, a regulated amount of the latter, from a previous operation, being mixed in with the new material to be treated.

The facts are quoted with interest in respect to the natural carbonate of soda held in solution by the water of Owens Lake, in Inyo County, California. Chatard's report estimating the total amount of this carbonate in the lake at 40 to 50 millions of tons—the product, so far obtained in a small way only, has the composition $Na_2CO_3.NaHCO_3.H_2O$, but can, of course, be converted into the normal carbonate by heating.

There is an account of Castner's new industrial product, sodium dioxide, likely to prove a valuable laboratory reagent, which is made, chiefly for use in bleaching, by the Aluminium Company (limited) of London and Oldbury—prepared by heating metallic sodium to 300° C. in vessels of aluminium, and passing over it at first air nearly deprived of oxygen, and at the end of the process air containing its full proportion of oxygen. The product is best applied in bleaching along with magnesium sulphate, so as to avoid the ill effects of the alkaline soda if unneutralized.

An interesting result is presented of the reduced demand for metallic sodium, due to aluminium being now made by electrolysis, in the application of the former metal to the manufacture of a mixed potassium and sodium cyanide (sold as "cyanide of potassium" for use in the metallurgy of gold) by the reaction.

$$K_4Fe(CN)_6 + Na_2 = Fe + 4KCN + 2NaCN,$$

which, unlike the older processes, avoids the formation of cyanate and utilizes the whole of the cyanogen present.

Under the head of "Produits chimiques et pharmaceutiques" are included all the finer chemicals, especially those of organic character. There is a passing remark on the difficulty in distinguishing at Chicago, in the American department, between products really made in the United States and those which American houses sent to the exhibition, although acting only as importers or agents for European firms.

The great activity shown of late years in the production of new medicinal agents, and in the investigation of their physiological effects, is commented upon, and a long list is presented of these substances, partly of natural origin, extracted from vegetable sources—new alkaloids, glucosides, etc.,—and partly prepared by synthetic laboratory methods. The enormous increase in the production of quinine, followed by a fall in price from 800 to 1,000 francs per kilogram thirty years ago to 30 or 40 francs now, is noted, and the occurrence at the Chicago exhibition of fine specimens of cupreine, the alkaloid from *Remigia pedunculata*, of which the relation to

quinine has been shown by Grimaux and Arnaud, quinine being methyl-cupreine. Sparteine, now applied to medical use, and gymnemic acid, from the leaves of *Gymnema sylvestris*, with its curious effect upon the nerves of taste, rendering them insensible to the impressions of bitter or sweet, are among the newer substances of natural origin which are mentioned. As regards chloroform, notice is taken of the now general practice of first independently preparing chloral and then decomposing it by an alkali, and also of the Pictet method of purifying chloroform by crystallizing it on exposure to very low temperature (the melting-point is—62° C.). But nothing is said as to the extensive substitution of acetone for alcohol as the prime material. Among the synthetic products for medical use are noticed diethylene-diamine (pipera zine) as a solvent for uric acid, and paraphenetol-carbamide (sucrol) as a sweetening material when sugar is to be avoided.

Attention is drawn to the extension and growing importance of photographic chemicals, and of those used as reagents in scientific laboratories and in analysis. There has been marked improvement of late years in the variety of these attainable, and in the purity of condition which many of them present as they can now be purchased.

Interesting little specialties are noted in the "artificial spindle oil" exhibited by the Russian firm of Krestovnikoff Brothers, of Kasan, an oleate of amyl, and the "lipogenine" of the same firm, a palmito-stearate of ethyl. These products suggest a comparatively little trodden path, the investigation of the various esters and other salts of the higher fatty acids, artificially produced. A step in the industrial application of such work was taken a number of years ago, when the *Aktien-Gesellschaft für Anilinfabrikation* of Berlin began to make their *Anilinfettfarben* for color-printing, salts of linoleic, etc. acids with the colored triamine bases, rosaniline, etc.

The report contains an extended discussion of the structure of the principal artificial coloring materials used in modern dyeing, and of the difficult question of general relation between structure and tinctorial properties, the reporter adopting provisionally Witt's classification of these materials in 17 groups. Reference is made, for the general history of this department of chemical industry, to Caro's admirable lecture before the German Chemical Society in 1892. The exhibition of coal-tar colors was not by any means so extensive and brilliant at Chicago as at several places at which previous expositions had been held; it is noted that there were but three European firms producing these colors represented, out of about thirty such firms in existence and at work. Among the newer materials of this kind are particularly noticed—new anthracene

blues, producing very fast tints on wool, which resist exposure to air, light, and washing with soap, fully replacing indigo in wool-dyeing—indoine, a derivative of pheno-safranine, giving good results resembling those of indigo on *cotton*—and some valuable new rhodamines. There was a fine display of artificial indigotine, and of the various materials which are required for its synthesis by different lines of approach.

Under the head of materials for perfumery it is remarked that France is still, as she has long been, the leading producer of natural perfumes of vegetable origin, but that of late years the cultivation of flowers, etc., for this use has been extended from the French Mediterranean coast to that of Algeria, where there are now large plantations under exceedingly favorable conditions as respects climate. The only essential oil mentioned, as produced in the United States, is that of mint; no notice is taken of other American specialties, such as sassafras and wintergreen (*gaultheria*). There a is decided advance reported in the production of artificial or synthetic perfumes—the isolation of irone, as the odorous principle of the iris and the violet, and the extraction from oil of lemon of citral, from which (itself a substance of but moderate cost) can be produced synthetically ionine, isomeric with irone, and having the same iris and violet odor—the production of aubepine (anisic aldehyde), neroline and yara-yara from β-naphthol, etc.

The report is sent out from the "*Imprimerie Nationale*," and illustrates the clearness and elegance of French typography. J. W. M.

The Density of Oxygen and Hydrogen; a Correction.

The scale of the barometer with which the pressures of the gases were measured in the experiments mentioned on page 274, was compared with two metres procured from the Société Genevoise, and accompanied with its statement purporting to give their true length. But both have now been compared with the Standards of the United States Coast and Geodetic Survey, with the result that the length certified by the maker is in error by 1/30000. The densities given for the gases should, therefore, be increased by 1/3000; when they become:

Density of oxygen, latitude 45° ... 1.42900 $\pm$0.000034
Density of hydrogen ..... 0.089873$\pm$0.0000027

The correction is, of course, smaller than the remaining uncertainty of the densities; but the corrected values are the actual results of the experiments. EDWARD W. MORLEY.